

FACILITATED TRANSPORT OF HYDROPHOBIC ORGANIC COMPOUNDS BY
COSOLVENT EFFECTS DUE TO OXYGENATED FUELS

By

COLIN SHIH-HSIEN CHEN

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1996

Dedicated to my grandfather

Mr. Wan-Lai Chen

A pioneer sanitary engineer in Taiwan

for his love and support

ACKNOWLEDGMENTS

I wish to express my grateful appreciation to my committee chairman, Dr. Joseph Delfino, and cochairman Dr. Suresh Rao. Dr. Delfino carefully guided my progress through the Master's and Ph.D. programs and secured my assistantship. He also helped me to obtain research funding throughout my study. Dr. Rao graciously offered the use of his laboratory and frequently provided probing questions and criticisms during my study. It is my privilege to be guided by these two advisors.

I would like to thank my committee members, Dr. Paul Chadik, Dr. Michael Annable, and Dr. Robert Kennedy for their technical and editorial support. In particular, I appreciate Dr. Chadik's assistance with the ultrafiltration apparatus used in the colloid study, and Dr. Kennedy's guidance in chemical separation theory.

I would also like to thank my former colleague, Dr. Edward Heyse, for his valuable comments in reviewing my proposal and enlightening discussions during my proposal preparation. Special thanks go to Ms. Dongping Dai for her assistance in the column experiment and valuable discussions. Mr. Heonki Kim frequently helped me in trouble shooting and kept me company while working at night in the laboratory. Mr. Larry Schwandes assisted me in organic carbon analyses. Mr. Liyong Li helped me for the Fortran programming and spill scenario simulation. I also received help from others, notably Ms. Sue Lee and Ms. Lane Evans for their assistance in laboratory work, data

collection, and editing during my research. The friendship of students in Black Hall and McCarty Hall was enjoyable.

This study was supported, in part, by the United States Air Force, Contract No. F42650-95-M-0036, through Hill Air Force Base. I would like to thank the contract manager, Dr. Dan A. Stone, for his assistance in funding the project.

Finally, this work would not have been possible without the love and support of my wife Rebecca and the joy my daughter Erica brings to our family. I also thank my parents and parents-in-law for their encouragement and financial support during my study.

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Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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By

Colin Shih-Hsien Chen

December, 1996

Chairman: Dr. Joseph J. Delfino

Cochairman: Dr. P. Suresh C. Rao

Major Department: Environmental Engineering Sciences

Oxygenated fuels have led to increased interest in the transport and fate of miscible organic liquids in the environment and the effect of these liquids on the transport and fate of other contaminants. Cosolvent-induced solubilization of hydrophobic organic compounds (HOCs) into water will increase the potential for secondary contamination in an impacted site. The objectives of this research were to study (1) the phase redistribution of hydrophobic organic compounds in aqueous and sediment/soil systems with simulated spills of oxygenated fuels in river and subsurface environments; and (2) the facilitated transport of HOCs by colloids in a sediment/water system where colloids serve as nucleating agents for condensing solutes as the cosolvent fraction is diluted during transport.

The cosolvent effect of oxygenated compounds (methanol, ethanol, and methyl tert-butyl ether (MTBE)) on the solubility and enhanced mobilization of polynuclear aromatic hydrocarbons (PAHs) was examined using laboratory experiments. Coal tar

contaminated sediment and soil were used to study the redistribution and facilitated transport of eighteen PAHs when oxygenated fuel spills occur. The results indicated that PAH solubility increased essentially in a log-linear manner with an increased volume fraction of methanol and ethanol. Deviations from a log-linear relationship were observed for MTBE due to its limited aqueous solubility, and the cosolvent effect was seen only at the simulated spill site. A log-linear relationship between the octanol/water partition coefficient and cosolvency power was observed. In column experiments, the elution profile of 18 PAHs suggested that oxygenated compounds from fuel can serve as cosolvents which will enhance the dissolution of PAHs from contaminated soil while the fuel makes contact with the contaminated soil.

The significance of the colloidal phase in the redistribution of PAHs in coal tar contaminated sediment/water system by introduction of oxygenated fuels was also evaluated. Ultrafiltration was employed to differentiate colloids from aqueous phase samples to examine the colloid-facilitated transport of PAHs in simulated fuel-spill systems. A three-phase distribution (sediment-colloidal-aqueous phase) was applied to study the redistribution of PAHs from coal tar contaminated sediment. The results showed that cosolvency was more significant than the role of colloids in the redistribution of PAHs because the cosolvent effect reduces the sorption of PAHs onto colloids.

This study provides a basis to predict the facilitated transport of HOCs from contaminated sediment and soil due to the cosolvent effects of oxygenated fuels. The fuel spill scenarios may assist in the further assessment of the environmental and health effects of spills and leaks of oxygenated fuels.

CHAPTER 1 INTRODUCTION

Oxygenated Fuels

Gasoline is a middle distillate of petroleum, containing C_4 to about C_{12} hydrocarbons. The major components are normal/iso hydrocarbons (55% volume percent), aromatic hydrocarbons (34%), cycloparaffins (5%), and olefins (5%) (Watts, 1986). Gasoline also includes a number of additives, such as antiknock agents, antioxidants, metal deactivators, corrosion inhibitors, surfactants, and octane enhancers (Cline et al., 1991). The use of high-octane oxygenated blending agents in gasoline has increased since 1975 (API, 1988). Oxygenates are liquid organic compounds that can be blended into gasoline to increase its oxygen content. During combustion, the additional oxygen in the gasoline reduces the output of carbon monoxide and may reduce the emissions of ozone-forming substances.

Three different alternative fuel programs have been mandated in the 1990 Clean Air Act Amendments to minimize combustion-related pollution.

(1) Reformulated gasoline must be available in the nine worst ozone non-attainment areas beginning in 1995. This must decrease emissions of volatile organic compounds (VOCs) and polynuclear aromatic hydrocarbon (PAH) emissions by 15 % by 1995 and 25% in 2000. A 2% year-round oxygen content is required in reformulated gasoline (Sawyer, 1993).

(2) Areas that do not meet Federal carbon monoxide standards must use oxygenated fuels during winter months. Gasoline in these areas must contain at least 2.7% oxygen by weight during winter months. Addition of oxygenates such as methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), or tert-butyl alcohol (i.e., tert-butanol, TBA) to gasoline provides the required oxygen. In the case of addition of MTBE, the 2.7% oxygen content requires 15% by volume of MTBE in gasoline (Anderson, 1993).

(3) New motor vehicle fleets must include a certain percentage of low-emission vehicles, especially those that can operate on reformulated gasoline, methanol, compressed natural gas, liquid petroleum gas, or other clean fuels (Chang et al., 1991).

The oxygenated gasoline used in this research contained 15% MTBE (by volume), and the alternative fuels M85 and E85 contained 15% gasoline and 85% methanol or ethanol by volume, respectively. The term, oxygenated fuel, was used to represent all the oxygenated gasoline and alternative fuels investigated in this study.

Impact of Oxygenated Fuel Spill on Existing Contaminated Sites

Oxygen-containing compounds such as MTBE are relatively soluble in water (43,000 mg/L). Benzene, toluene, ethylbenzene, and xylenes (BTEX) in gasoline are more soluble in MTBE than they are in water. When gasoline containing MTBE leaks into groundwater, the MTBE spreads further and faster than gasoline components. Therefore, the concentration of gasoline components dissolved in groundwater will increase (Garrett et al., 1986).

There is little information regarding the effect of oxygenated fuels on the transport and fate of hydrophobic organic compounds (HOCs). When an oxygenated fuel spill

occurs, the HOCs of the oxygenated fuel will be retained by the soil, however, the soluble contaminants will show high mobility in conjunction with surface water/groundwater flow. Uncontaminated surface water or groundwater will continuously flow into and through a plug of spilled oxygenated fuel and/or its downstream plume. Because the composition of the fuel phase will change as a result of dissolution of the soluble components, the aqueous concentrations of BTEX will change by the successive flow of uncontaminated water. For the purposes of this study, such phenomena are termed primary contamination.

When spilled oxygenated fuels encounter contaminated soil, sediment or aquifer material, the aqueous concentrations of HOCs that previously had sorbed onto soil/sediment may increase by orders of magnitude due to the enhancement of solubility and decreased sorption induced by the miscible oxygenated compounds from oxygenated fuels. This phenomenon is defined here as secondary contamination. Examples of the common HOCs that could be mobilized with an oxygenated fuel spill in certain settings are polynuclear aromatic hydrocarbons (PAHs). These contaminants have relatively low aqueous solubilities and are widely distributed in the environment, sorbed onto soil, sediment, or aquifer materials. Therefore, cosolvent-induced solubilization of HOCs into the aqueous phase will increase the potential for secondary contamination.

In evaluating the oxygenated fuel contamination described above, several important questions arise and these are framed as hypotheses:

- (1) The solubility enhancement of HOCs is significant in terms of increasing the magnitude of contamination.
- (2) Facilitated transport of HOCs will be seen at the fuel contaminated site.

- (3) Oxygenated compounds will have the opportunity to cause secondary contamination in surface and subsurface environments.

To address these hypotheses and assess the potential problem of secondary contamination, it is essential to evaluate current conditions of contaminated sites. These issues will be addressed in the following sections.

Approximately 3.5 million underground storage tanks (UST) are used to store petroleum products, chemicals, hazardous wastes, and other liquids in the United States (1.4 million USTs for gasoline). Based on conservative estimates, 10% of them may leak their contents to the surrounding environment (Dowd, 1984; Federal Register, 1987). Since UST systems for gasoline and diesel fuels (diesel fuel has a high PAH content) at service stations are generally close to each other, the potential for simultaneous or sequential leaks is high.

The U.S. Environmental Protection Agency (EPA) estimates that there are more than 650,000 on-shore oil storage facilities nationwide with above ground oil storage tanks (USGAO, 1989). To facilitate transportation of petroleum products, the petroleum industry frequently locates storage facilities along coastal and inland waterways. Thus, the spills from these facilities can contaminate the aquatic environment. Since 1982, 2,000 to 3,000 oil spills originating from oil storage facilities have been reported to the federal government annually. For instance, about one million gallons of diesel fuel spilled into the Monongahela River when an above ground oil storage tank collapsed in 1988 in Floreffe, Pennsylvania. In the same year, 400,000 gallons of crude oil leaked into a waterway near San Francisco Bay from a storm water drainage system at a Shell Oil Company facility above-ground storage tank (USGAO, 1989).

Contamination at petroleum processing facilities and oil terminals can involve a variety of petroleum products such as crude oil, gasoline, oxygenated fuels, diesel fuel, heating oil, etc. These fuels contain a wide range of HOCs, any one of which is subject to cosolvent effects of oxygenated fuels when spills occur. Also, transportation of fuels creates a significant potential for the accidental discharge of petroleum products onto land.

With the potential problems as described above, clean-up operations involving oxygenated fuel spills may deal with more contaminants and higher aqueous concentrations than expected. The leak or spill of an oxygenated fuel may complicate the processes and increase the costs for clean-up and remediation. To predict the fate parameters (i.e., dissolution, sorption) that might be used in regulatory decisions and health concerns, it is essential to study the cosolvent effect of oxygenated fuels on HOCs in soil/sediment systems.

Fuel Spill Scenarios

Because oxygenated fuels are comprised of some highly-volatile and soluble hydrocarbons and oxygenated compounds, their transport in surface and subsurface aquatic systems can occur in more than one fluid phase. Fuel components can move as dissolved solutes in the water phase, free product in the immiscible phase, and vapor in the gaseous phase. Multi-phase flow is complicated by different characteristic properties which govern the transport of components through surface or groundwater systems (Freeze and Cherry, 1979). Thus, the hypothetical oxygenated fuel spill scenarios in the surface and subsurface aquatic systems were established to assist the understanding of secondary contamination.

An example of oxygenated fuel contamination in a surface water system is illustrated in Figure 1-1. The spills of oxygenated fuels in the river involve two-phase plumes (water miscible and immiscible plumes). The immiscible plumes are contributed by fuel constituents (e.g., BTEX) and oxygenated compounds are miscible plumes. Oxygenated compounds have low densities (e.g., $\rho_{\text{methanol}} = 0.796 \text{ g/mL}$, $\rho_{\text{ethanol}} = 0.794 \text{ g/mL}$, and $\rho_{\text{MTBE}} = 0.744 \text{ g/mL}$) relative to water and are completely miscible or highly soluble in water. For an oxygenated fuel spill in a river, water contaminated with oxygenated compounds will be characterized by completely dissolved contaminants, and will exhibit a density less than the density of uncontaminated river water. When gasoline constituents encounter water, these compounds will spread and form a thin oil film on top of the surface water due to the immiscibility between the hydrophobic components and difference of surface tension. The thin film will move downstream by hydrodynamic forces. In the case of a large spill of oxygenated fuel, the low-density and miscible components act as a large mass of liquid. After the oxygenated compounds completely dissolve in water (the equilibration rate is relatively fast), the dissolved contaminant plume will have a density between that of the pure oxygenated compound and that of river water. The dissolved contaminant plume will tend to mix through the water column and finally reach the bottom sediment. The low-density miscible plume will have migrated a great distance from the spill area, and the effect of hydrodynamic dispersion will be to dilute the plume, resulting in a lower volume fraction of cosolvent and a fluid density gradually approaching that of water. The immiscible plume (fuel-related hydrocarbons) will tend to float on surface water and travel further distances downstream.

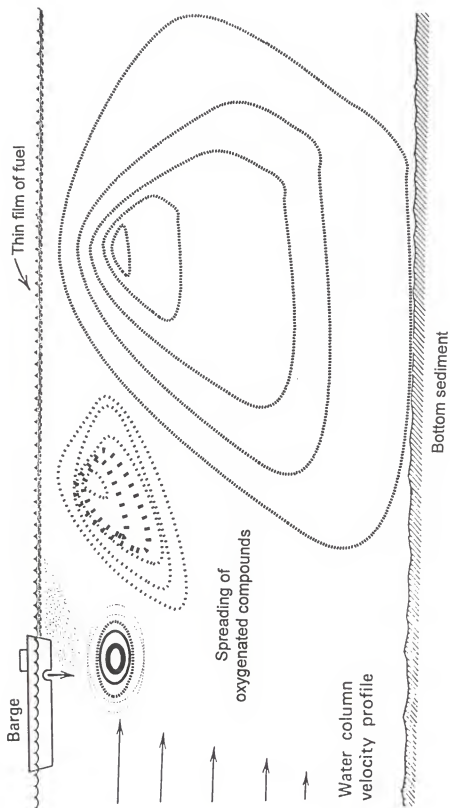


Figure 1-1. Hypothetical representation of an oxygenated fuel spill in a surface water system.

Just as in the case of a spill into a surface water system, spills of oxygenated fuels in the subsurface environment also involve miscible and immiscible plumes. In the subsurface environment, a plume contaminated with oxygenated compounds will be characterized by completely dissolved contaminants and will exhibit a density less than the density of uncontaminated water (Figure 1-2). Due to the properties of low density and infinite or high solubility, oxygenated compounds display a range of behavior when encountering groundwater. In the case of a large spill of oxygenated fuel, the low-density and miscible contaminants reach the water table as a large mass of liquid. The low density of the liquid will prevent the immediate mixing of the contaminant into the groundwater. The contaminant liquid will tend to pool on the water table surface with mixing occurring at the interface between the contaminant pool and the groundwater.

After the oxygenated compounds completely dissolve in groundwater, the contaminant plume will have a density between that of the pure oxygenated compound and that of groundwater. Large concentrations of oxygenated compounds in the dissolved plume will result in lower plume densities. Thus, there will be a greater tendency for the plume to remain at the top of the aquifer as it is advected along with the groundwater flow. After a low-density miscible plume has migrated a great distance from the source area, the effect of hydrodynamic dispersion will have diluted the plume, resulting in a density near that of the original groundwater. Also, the process of transverse dispersion will have contributed to the vertical spreading of the plume. At great distances from the source area, the plume will extend from the top of the aquifer to a depth greater than which observed near the source. Depending on the migration distance and the thickness of the aquifer, contamination may extend over the entire vertical thickness of the aquifer.

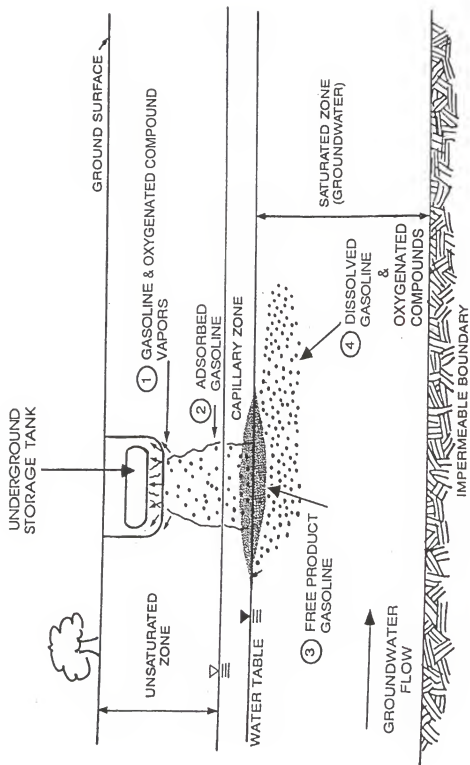


Figure 1-2. Hypothetical representation of an oxygenated fuel spill in the subsurface environment.

The immiscible plume (fuel-related hydrocarbons) will tend to float on water due to its low density. The floating plume will be found at or near the water table and may locally disperse along the water table. The movement is controlled by gravity and the advective groundwater velocity.

Research Objectives

The focus of this research project was to investigate the redistribution and facilitated transport of HOCs from contaminated sediment/soils caused by cosolvent effects due to oxygenated fuel spills. Recall the hypotheses presented earlier on Page 3. Specifically, the objectives were to:

- (1) Study the phase redistribution of HOCs in aqueous, colloidal, and sediment systems upon the addition of oxygenated fuels. It is hypothesized that the cosolvent-induced solubilization of HOCs into water will increase the potential of secondary contamination at an impacted site.
- (2) Study the enhanced mobilization of HOCs by colloids in simulated spills within a river system where colloids serve as nucleating agents for condensing solutes as the cosolvent fraction is diluted during transport.
- (3) Investigate the dissolution and facilitated transport of PAHs from contaminated soil caused by cosolvent effects due to oxygenated fuel spills in the subsurface environment.

CHAPTER 2

FACILITATED SOLUBILIZATION OF POLYNUCLEAR AROMATIC HYDROCARBONS BY THE COSOLVENT EFFECT OF OXYGENATED FUELS

Introduction

The use of high-octane oxygenated blending agents in gasoline has increased since 1975 (API, 1988). Oxygenates are liquid organic compounds that can be blended into gasoline to increase its oxygen content. During combustion, the additional oxygen in the gasoline reduces the output of carbon monoxide and may reduce the emissions of ozone-forming materials.

Oxygenated fuels became popular because three different alternative fuel programs have been mandated in the 1990 Clean Air Act Amendments to minimize combustion-related pollution (Chang et al., 1991; Anderson, 1993). These fuels have brought increased interest in the transport and fate of miscible (completely and partially) organic liquids in the environment and the effect that these liquids have on the transport and fate of other contaminants (Brusseau, 1993). The addition of polar organic solvents that are completely miscible or highly soluble in water to a mixture of hydrocarbons and water has the potential of showing the cosolvent effect (Fu and Luthy, 1986a; Munz and Roberts, 1986; Groves, 1988; Pinal et al., 1990; 1991). A cosolvent may affect the aqueous cavity surrounding a solute, therefore, changing the energetic cost of forming such a cavity. Cosolvency is defined as the effect of organic solvents on the solubility

and sorption of HOCs (Rao et al., 1990). This can be described by the following observations: (1) methanol and ethanol, as water-miscible cosolvents, may reduce the net polarity of the oxygenate-water solvent. When a miscible constituent (cosolvent) is added to water, it increases the quantity of nonionic organic compounds that can dissolve in the mixed solvent. For example, the presence of the cosolvent in an oxygenated fuel (e.g., M85, which is 85% methanol and 15% gasoline) could enhance the transport of the gasoline constituents contained in the fuel when a fuel spill occurs. Thus, the potential for gasoline contamination will increase; (2) Sorption will decrease in a log-linear manner upon addition of a cosolvent (Rao et al., 1985; Nkedi-Kizza et al., 1985; Fu and Luthy, 1986b); and (3) The addition of cosolvents has been shown to increase mass transfer rates in sorption (Nkedi-Kizza et al., 1989; Brusseau et al., 1991; Augustijn et al., 1994). Therefore, the use of oxygenated fuels leads to cosolvency becoming an important issue.

There is little information regarding the effect of oxygenated fuels on the transport and fate of HOCs. When an oxygenated fuel spill occurs, the HOCs in the fuel will be retained by the soil; however, the soluble contaminants will show high mobility in conjunction with surface water/groundwater flow. Uncontaminated surface water or groundwater will continuously flow into, and through, a pulse of spilled oxygenated fuel and/or its downstream plume. Because the composition of the fuel phase will change due to dissolution of the soluble components, the aqueous concentrations of benzene, toluene, ethyl benzene, and xylenes (BTEX) will also be changed by successive flow-through of uncontaminated water. For the purposes of this study, such phenomena represent primary contamination of the water.

When spilled oxygenated fuels encounter soil, sediment or aquifer material contaminated with HOCs, the aqueous concentrations of HOCs that previously had sorbed onto soil/sediment may substantially increase due to the enhancement of solubility by miscible oxygenated compounds present in the fuels. The common HOCs that could be mobilized with an oxygenated fuel spill in certain settings are polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). These contaminants have relatively low aqueous solubilities and are widely spread in the environment, sorbed onto soil, sediment, or aquifer materials. The solubilization of these previously sorbed HOCs represents what we call secondary contamination. Therefore, cosolvent-induced solubilization of HOCs into the aqueous phase will increase the potential for secondary contamination. With the potential problems as described above, clean-up operations involving oxygenated fuel spills may deal with more contaminants and higher aqueous concentrations than expected. Therefore, the leak or spill of an oxygenated fuel may increase the difficulty of clean-up and remediation. To predict the fate parameters (e.g., dissolution, sorption) that might be used in regulatory decisions and health concern, it is essential to study the cosolvent effect of oxygenated fuels on HOCs that may be associated with soil/sediments.

The objective of this research was to investigate the redistribution and facilitated transport of HOCs from contaminated sediment caused by cosolvent effects due to oxygenated fuel spills. Specifically, the phase redistribution of HOCs in aqueous and sediment systems upon the addition of oxygenated fuels was studied. The results are

expected to allow further assessment of the environmental and health effects of spills and leaks of oxygenated fuels.

Theory

The effect of oxygenated organic liquids (cosolvents) on the solution-phase activity of organic compounds depends upon the nature of the solute and solvent-cosolvent system. A simple relationship describing the influence of cosolvent on the solubility of a solute in the mixed-solvent system is the log-linear cosolvency model (Yalkowsky et al., 1972; 1976; Yalkowsky and Rubino, 1985; Fu and Luthy, 1986a; Pinal et al., 1990):

$$\log S_m = \log S_w + \sigma f_c \quad (2-1)$$

where S is the solubility of the solute in water (w) and mixed-solvent (m), f_c is the volume fraction of organic cosolvent in the aqueous phase, and σ represents the cosolvency power of the cosolvent. Similarly, for the system with multiple cosolvents, eq (2-1) becomes:

$$\log S_m = \log S_w + \sum \sigma_i f_i \quad (2-2)$$

This equation predicts that $\log S_m$ will vary linearly with f_i if all other conditions are held constant (Morris, et al., 1988). When water-cosolvent interactions are significant, deviations are found from the log-linear solubility profiles predicted by eq (2-1). Deviations are quantified by the degree of nonideality of the solvent mixture (Baberjee and Yalkowsky, 1988). Such water-cosolvent interactions can be accounted for by an empirical term β (Rao et al., 1991). Thus, eq (2-1) is modified as the following equation:

$$\log S_m = \log S_w + \beta \sigma f_c \quad (2-3)$$

where β is an empirical coefficient that accounts for water-cosolvent interactions so that $\beta\sigma$ expresses the overall cosolvency power, all others are defined as in eq (2-1). The degree of nonideality varies with cosolvent content, and therefore the use of a constant β is only an approximation of more complex behavior. Usually β can be considered as a constant larger than 1.0 up to a cosolvent fraction of 0.5, after which it normally decreases back to a value of 1.0 (Augustijn et al., 1994).

The cosolvency power can be viewed as the hypothetical partition coefficient for the HOCs between a cosolvent and water (Rao et al., 1990). The logarithm of the ratio of HOC solubilities in pure cosolvent and in pure water (S_w) is equal to the cosolvency power (σ):

$$\sigma = \log (S_c/S_w) \quad (2-4)$$

where S_c is the solubility of the solute in pure cosolvent.

A correlation between the cosolvency and a HOC's octanol-water partition coefficient (K_{ow}) was established as follows (Morris et al., 1988):

$$\sigma = a \log K_{ow} + b \quad (2-5)$$

where K_{ow} is the octanol-water partition coefficient and both of a and b are constants applying to a group of compounds. Substituting the expression for σ from eq (2-4) into eq (2-1) gives:

$$\log S_m = f_c \log S_c + (1-f_c) \log S_w \quad (2-6)$$

Sorption of HOCs is inversely related to solubility. Thus, an increase in solubility resulting from the addition of a cosolvent leads to a proportional decrease in sorption.

For the sorption of HOCs from aqueous-organic binary solvent mixtures, the sorption coefficient is predicted to decrease exponentially as the fraction of organic solvent increases. A log-linear cosolvency model has been established to relate the equilibrium sorption coefficient (K_p) to the volume fraction of cosolvent from binary mixed solvent (Rao et al., 1985; 1990). The equation is expressed as:

$$\log K_{p,b} = \log K_{p,w} - \sigma f_c \quad (2-7)$$

where $K_{p,b}$ and $K_{p,w}$ are the equilibrium sorption constants for the binary solvent and aqueous systems, respectively, and σ is the cosolvency power of the cosolvent. The addition of a cosolvent will result in a decrease in retardation and a decrease in the sorption coefficient (K_p). Such phenomena have been frequently demonstrated (Fu and Luthy, 1986b; Nkedi-Kizza et al., 1985; 1987; 1989). For a mixture of water and multiple cosolvents, eq (2-7) may be extended as follows:

$$\log K_{p,m} = \log K_{p,w} - \sum \sigma_i f_i \quad (2-8)$$

where m denotes the mixed solvent and i is the " i "th cosolvent, with the other terms as defined earlier. A correction factor (α) can be introduced to account for nonideal behavior due to the cosolvent-sorbent interactions (Rao et al., 1985; Kimble and Chin, 1994). Thus, eq (2-8) becomes:

$$\log K_{p,m} = \log K_{p,w} - \alpha \beta \sigma f_c \quad (2-9)$$

where α is a nonideality coefficient that accounts for cosolvent-sorbent interactions, with β defined in eq (2-3), $\alpha \beta \sigma$ represent the overall cosolvency power for the partition of HOCs between soil and solvent, and the rest of the terms are defined in eq (2-7). The theoretical value of α for most HOCs can be roughly estimated (Kimble and Chin, 1994).

It was found α will be smaller for more polar compounds, while less polar compounds will have values closer to unity (i.e., $\alpha=1.0$).

Materials and Methods

Coal tar contaminated sediment from Harbor Point, New York was used to study the redistribution of polynuclear aromatic hydrocarbons (PAHs) in sediment and aqueous phases in a simulated river system. The physical and chemical properties of the contaminated sediment were determined prior to the initiation of experiments. Eighteen target polynuclear aromatic hydrocarbon (PAH) compounds were studied (Table 2-1) and the numbering sequence in Table 2-1 is used throughout this dissertation. Based on a chemical characterization of the sediment, the total PAH content (sum of eighteen PAHs) in the coal tar contaminated sediment was approximately 800 mg/kg. The oxygenated compounds used in the study were methanol, ethanol, and methyl tert-butyl ether (MTBE). Unleaded gasoline (93 octane) was obtained from a local service station. Gasoline composition was monitored prior to each experiment to make sure none of the above additives were in the gasoline. Oxygenated fuels were prepared by mixing gasoline and oxygenated compounds in the laboratory. Oxygenated fuels selected in this study included two alternative fuels (M85 and E85) and oxygenated gasoline. The M85 and E85 were specifically selected as the alternative fuels to evaluate their performance under the original guidelines of the Alternative Motor Fuels Act of 1988 and the Energy Policy Act of 1992. These alternative fuels have been studied by car manufacturers under the alternative fuel vehicle program for the purpose of reducing emissions (AFDC

Table 2-1. Selected properties of PAH compounds investigated in this study.

Compound	MW (g/mole)	mp ^a (°C)	Solubility ^a (mg/L)	log K _{ow} ^a
1. naphthalene	128.18	80.5	32	3.36
2. 2-methylnaphthalene	142.20	34.6	26	3.86
3. 1-methylnaphthalene	142.20	-22	27	3.87
4. acenaphthylene	152.20	92-93	3.93	4.07
5. acenaphthene	154.21	95	3.47	3.92
6. fluorene	166.22	116.5	1.9	4.18
7. phenanthrene	178.24	98-100	1.18	4.52
8. anthracene	178.24	216.3	0.073	4.54
9. fluoranthene	202.26	107	0.26	5.22
10. pyrene	202.26	149-151	0.16	5.18
11. benzo(a)anthracene	228.30	155-157	0.010	5.61
12. chrysene	228.30	254	0.006	5.61
13. benzo[b]fluoranthene	252.32	163-165	0.014	6.57
14. benzo[k]fluoranthene	252.32	217	0.00055	6.85
15. benzo[a]pyrene	252.32	179	0.003	6.04
16. indeno[1,2,3-cd]pyrene	276.34	160-163	0.062	7.70
17. dibenzo[a,h]anthracene	278.35	269-270	0.0005	6.36
18. benzo[ghi]perylene	276.34	278-280	0.00026	7.10

a Groundwater Chemicals Desk Reference, Montgomery and Welkom (1990).

Update, 1996). The M85 and E85 fuels contain 15% gasoline, and 85% methanol or ethanol, respectively. The oxygenate, MTBE, was added to gasoline to a total of 15% by volume to form the oxygenated gasoline.

Sediment/Water Partition Experiment

The partitioning behavior of multicomponent liquids in water or water-miscible solvents has been addressed in several studies (Cline et al., 1991; Lane and Loehr, 1992; Lee et al., 1992a; 1992b; Chen et al., 1994; Peters and Luthy, 1993; 1994). These studies employed the Raoult's law convention for activity coefficient calculations in conjunction with liquid or supercooled liquid solubilities to estimate aqueous-phase concentrations of aromatic hydrocarbons. The Raoult's law-based approach can be adopted to evaluate the redistribution of PAHs in different phases due to the cosolvent effect of oxygenated fuels.

The equilibrium concentrations of PAHs in sediment/water systems were determined by batch partition experiments. The experimental setup was run in six replicates. Approximately ten grams of coal tar contaminated sediment were placed in a reaction vial containing 40 mL of deionized (D.I.) water with 0.01 N calcium chloride to equilibrate for 24 hours on a shaker at room temperature ($22\pm 2^\circ\text{C}$). The calcium chloride was used to improve sediment particle coagulation and settling after attaining equilibrium. After shaking, the aqueous and sediment phases were separated by centrifugation (400 g). The 40 mL aqueous sample was extracted three times with 10 mL of methylene chloride. The extracts were dried by passing through a sodium sulfate column to remove residual water, and the extract volume was concentrated to 3-5 mL.

using a rotary evaporator. The extract volume was further reduced under a gentle stream of nitrogen to 1 mL, transferred to 1 mL crimp-seal vials and refrigerated (4°C) until analysis. The extracts were analyzed by gas chromatography/mass spectrometry (GC/MS). A partition coefficient (K_{sw}) that expresses the relationship between component concentration in sediment (C_s) and the aqueous phase (C'_w) was calculated for 18 PAH compounds:

$$K_{sw} = C_s / C'_w \quad (2-10)$$

Batch Dilution Experiment

Potential spills of oxygenated fuels in surface water/sediment systems were simulated in the laboratory. Equilibrium concentrations of PAHs in sediment/water systems were determined by sequential batch dilution. This experimental design represents the dilution effect in a river system in the event of an oxygenated fuel spill. Fuel/water ratios of 1:1 (representing the spill site) were used in the batch equilibration experiments to demonstrate a “worst case” scenario. Five grams of contaminated sediment, 20 mL of oxygenated fuel, and 20 mL of water were placed in a 50 mL Kimax centrifuge tube equipped with a cap with a Teflon liner septum. Equilibration time was 2 hours for each set of batch equilibrations. The vials were agitated on a shaker tray (horizontal shaking) at room temperature (22±2°C). After shaking, the separate fuel, aqueous, and sediment phases were collected from the reaction tubes. Aqueous samples (12 mL) were then taken for analysis. The second aqueous sample (8 mL) was placed in a new reaction tube containing 12 mL of fresh D.I. water and 5 g of new sediment. The

resulting mixture was equilibrated for 2 hours. Again, 12 mL of aqueous sample were taken for analysis and 8 mL of aqueous sample went into the next tube. Due to the complex nature of contaminated sediment, sediment samples from each batch experiment were taken for analysis to estimate the equilibrium concentration with the influence of cosolvent. Such water/sediment equilibrations were repeated three times to allow water (which contained the oxygenated compound) from the spill site to contact new sediment, and represented an approximate dilution effect of the cosolvent in the river system. Each experimental setup was run in triplicate. The redistribution of contaminants (PAHs) in the different phases by cosolvent-induced solubility enhancement was evaluated. The advantage of using batch dilution systems is that equilibrium conditions can be better approximated and the mass balance of PAHs can be more readily established.

The aqueous concentrations of PAHs in binary solvent mixtures (i.e., methanol/water or ethanol/water) were also determined in batch experiments. Instead of using mixed oxygenated fuels, individual oxygenated compounds (i.e., methanol, ethanol, MTBE) were used separately in equilibration with water and sediment. The experimental protocol was consistent with the batch experiments using the same volume ratio (1:1, oxygenate/water). The equilibration time and sample analysis were identical to previous batch experiments. These experiments served as a basis for comparison to evaluate the cosolvent effect (i.e., cosolvency power $\equiv \alpha\beta\sigma$) of oxygenated compounds for each HOC present in the coal tar sediment without the presence of fuel components.

PAH Analysis

Sediment phase samples from the batch dilution experiments were extracted using a batch extraction method (Chen, et al., 1996). Approximately 5 g of coal tar contaminated sediments were placed in 50-mL Kimax tubes, and sequentially extracted with 1:1 v/v methanol-methylene chloride. The first extraction step involved equilibration with 25 mL of the solvent mixture for one day on a rotary shaker. Two sequential extractions involved equilibrations with 10 mL of the solvent mixture. After each extraction step, the soil was centrifuged for 30 min, and the supernatant was passed through a Teflon® filter (0.20 µm). Extracts were passed through a sodium sulfate column to remove residual water and then stored in bottles with Teflon® lined septa at 4°C.

The aqueous samples from the batch dilution experiments were extracted using separatory funnels with 2 mL of methylene chloride (three times) and followed by rotary evaporation and passing extracts through sodium sulfate columns to remove residual water. The extract volume was further reduced by gentle nitrogen evaporation to 1 mL. The extracts were transferred to 1 mL crimp-seal vials with Teflon® lined septa and refrigerated (4°C) until analysis.

The sediment and aqueous extracts were analyzed using a Perkin-Elmer 8500 gas chromatograph/ion trap detector (GC/ITD) equipped with a Perkin Elmer AS 8300 autosampler. The GC column was a 0.25 mm i.d., 30 meter, fused silica XTI-5(5% diphenyl-95% dimethyl polysiloxane) column with a 0.5 µm film thickness (Restek corp). The temperature gradient consisted of a 4 min hold time at 60°C, a ramp to 120°C at 7°C/min followed by a ramp to 270°C at 10°C/min, and a final ramp to 300°C at

30°C/min with an 17 min hold time. Both injector and detector temperatures were maintained at 250°C. The acquisition parameters for the ITD were as follows: mass range 45-450 amu, target 21700, scan rate 0.50 s, acquisition time 47 min, filament delay 300 sec, mass defect 100 amu/100 amu, background mass 45 amu, electron energy 70 eV, electron multiplier voltage 1500 V, and transfer line temperature is 250°C. Analytical standards were measured at the beginning of each series of analyses. Internal standard calibration was performed during the GC/ITD analyses.

Results and Discussion

Sediment/Water Partition Experiment

The measured partition coefficients (K_{sw}) for PAHs in sediment-water system were calculated using eq (2-10). The partition coefficients (K_{sw}) for the PAHs in batch sediment/water systems, as well as their respective partition coefficients in octanol-water systems (K_{ow}) taken from the literature (Montgomery and Welkom, 1990), are shown in Table 2-2. The K_{sw} values were expected to show greater variation than parameters like K_{ow} , because of the complexity in the sediment composition. There was considerable variability in the concentrations of PAH constituents measured in the contaminated sediment. The variability of sediment phase PAH concentrations was about 15% and for the aqueous phase concentrations, it ranged between 5 to 10%, among the six replicates for each phase. It was observed that the more hydrophobic the compound is, the higher the variability in measured K_{sw} values.

Table 2-2. Partition coefficients of PAHs in a coal tar contaminated sediment-water system.

Compound	Sediment phase concentration C_s (mg/kg) ^a	Aqueous phase concentration C'_w (mg/L) ^a	Average Partition coefficient K_{sw}	log K_{sw}	log K_{ow} ^b
naphthalene	89.3–105.9	$5.10 \cdot 10^{-2}$ – $8.91 \cdot 10^{-2}$	$1.40 \cdot 10^3$	3.15	3.36
2-methylnaphthalene	78.1–95.3	$4.99 \cdot 10^{-3}$ – $7.20 \cdot 10^{-3}$	$1.62 \cdot 10^4$	4.21	3.86
1-methylnaphthalene	76.0–82.6	$4.34 \cdot 10^{-3}$ – $6.00 \cdot 10^{-3}$	$1.66 \cdot 10^4$	4.22	3.87
acenaphthylene	16.3–23.8	$9.21 \cdot 10^{-4}$ – $1.14 \cdot 10^{-3}$	$2.07 \cdot 10^4$	4.32	4.07
acenaphthene	31.240.3	$9.02 \cdot 10^{-3}$ – $1.27 \cdot 10^{-2}$	$3.60 \cdot 10^3$	3.56	3.92
fluorene	31.4–41.9	$3.81 \cdot 10^{-3}$ – $6.37 \cdot 10^{-3}$	$6.87 \cdot 10^3$	3.84	4.18
phenanthrene	76.3–88.0	$5.45 \cdot 10^{-3}$ – $8.94 \cdot 10^{-3}$	$1.26 \cdot 10^4$	4.10	4.52
anthracene	21.3–30.2	$2.92 \cdot 10^{-3}$ – $6.02 \cdot 10^{-3}$	$6.81 \cdot 10^3$	3.83	4.54
fluoranthene	51.4–62.9	$1.92 \cdot 10^{-3}$ – $2.54 \cdot 10^{-3}$	$2.36 \cdot 10^4$	4.37	5.22
pyrene	85.6–97.1	$2.19 \cdot 10^{-3}$ – $3.63 \cdot 10^{-3}$	$3.55 \cdot 10^4$	4.55	5.18
benzo(a)anthracene	33.1–44.7	$1.60 \cdot 10^{-4}$ – $2.11 \cdot 10^{-4}$	$2.06 \cdot 10^5$	5.31	5.61
chrysene	30.9–40.4	$6.32 \cdot 10^{-5}$ – $8.80 \cdot 10^{-5}$	$4.76 \cdot 10^5$	5.68	5.61
benzo[b]fluoranthene	17.9–28.0	$1.66 \cdot 10^{-5}$ – $2.47 \cdot 10^{-5}$	$1.13 \cdot 10^6$	6.05	6.57
benzo[k]fluoranthene	14.5–19.2	$1.74 \cdot 10^{-5}$ – $2.74 \cdot 10^{-5}$	$7.34 \cdot 10^5$	5.87	6.85
benzo[a]pyrene	22.2–27.1	$3.66 \cdot 10^{-5}$ – $6.56 \cdot 10^{-5}$	$4.84 \cdot 10^5$	5.69	6.04
indeno[1,2,3-cd]pyrene	12.7–18.6	$5.71 \cdot 10^{-6}$ – $4.57 \cdot 10^{-5}$	$1.11 \cdot 10^6$	6.05	7.70
dibenzo[a,h]anthracene	7.38–10.1	$1.32 \cdot 10^{-5}$ – $1.81 \cdot 10^{-5}$	$5.06 \cdot 10^5$	5.70	6.36
benzo[ghi]perylene	14.4–20.1	$5.83 \cdot 10^{-6}$ – $1.75 \cdot 10^{-5}$	$1.57 \cdot 10^6$	6.20	7.10

a. Range for analyses of six replicates.

b. Data from Groundwater Chemicals Desk Reference, Montgomery and Welkom (1990).

Solubility Enhancement

The concentrations of PAHs in the sediment and the aqueous phases after equilibration with M85, E85, and oxygenated gasoline are shown in Figure 2-1. Based on these results, the cosolvency power (σ) of oxygenated compounds was calculated to determine the degree of solubility enhancement.

To measure the incremental change of PAH concentrations in the aqueous phase caused by the cosolvent effect, the equilibrium aqueous concentrations of the PAHs (C'_w) were estimated by using sediment phase concentrations (C_s) of PAHs and the partition coefficients (K_{sw} , eq (2-10)) under the condition of no cosolvent added to the sediment/water systems. The cosolvency power (σ) was calculated using eq (2-1). The difference between the logarithm of aqueous phase concentrations of PAHs (C_m) in oxygenated compound/water mixtures (measured from the batch dilution experiment) and the logarithm of equilibrium aqueous concentrations (C_w) was divided by the volume fraction of cosolvent (f_c) to obtain the cosolvency power (σ). Since the experimental design allowed the formation of different volume fractions of cosolvent in sediment/water systems (dilution effect), the calculation of average cosolvency power was based on the results of different volume fractions of cosolvent present in the system (e.g., the volume fractions of methanol were 0.46, 0.18, and 0.074, respectively).

Measured solubilization profiles of PAHs in M85-water, E85-water, and oxygenated gasoline-water mixtures are plotted in Figure 2-2. Aqueous concentrations of PAH in the various binary cosolvent-water mixtures show a reasonable log-linear relationship according to eq (2-1). These results suggest that the more hydrophobic the

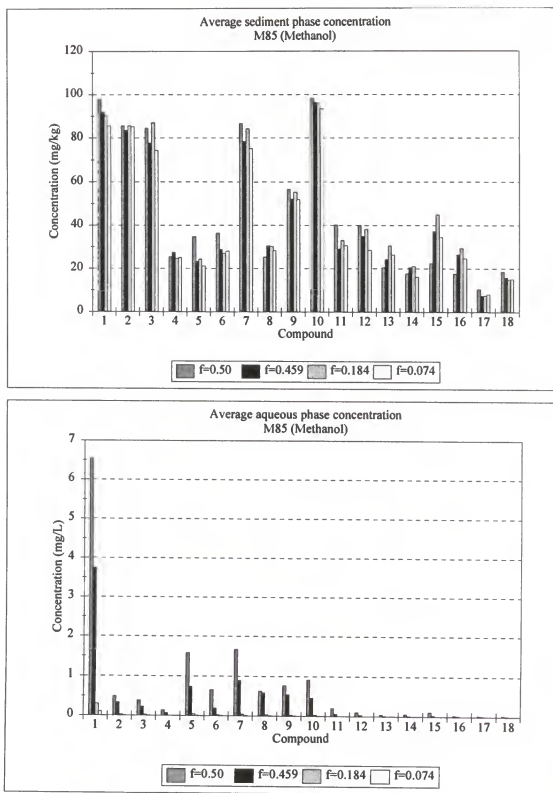


Figure 2-1. Average concentrations of PAHs in sediments and aqueous phases after equilibration with M85, E85, and oxygenated gasoline.

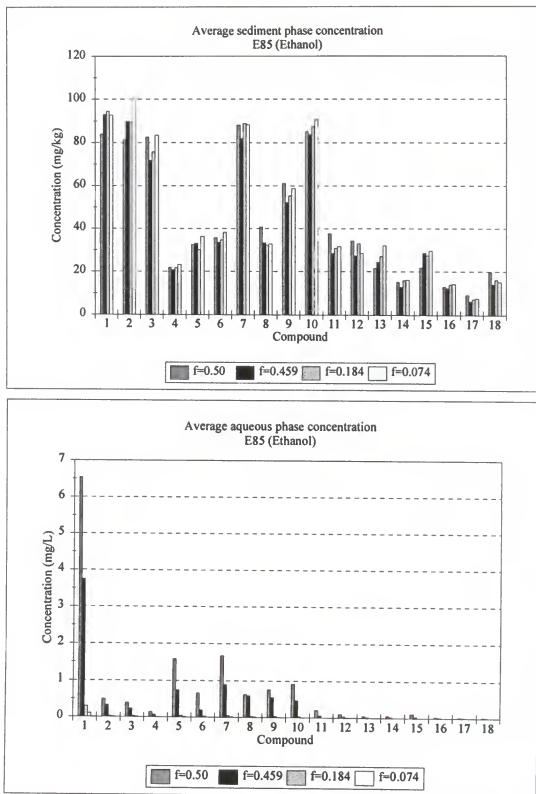


Figure 2-1. (Continued).

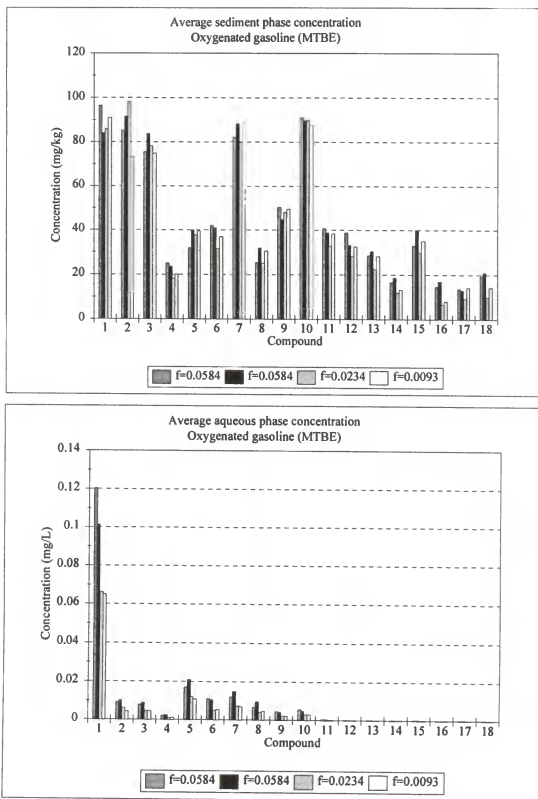


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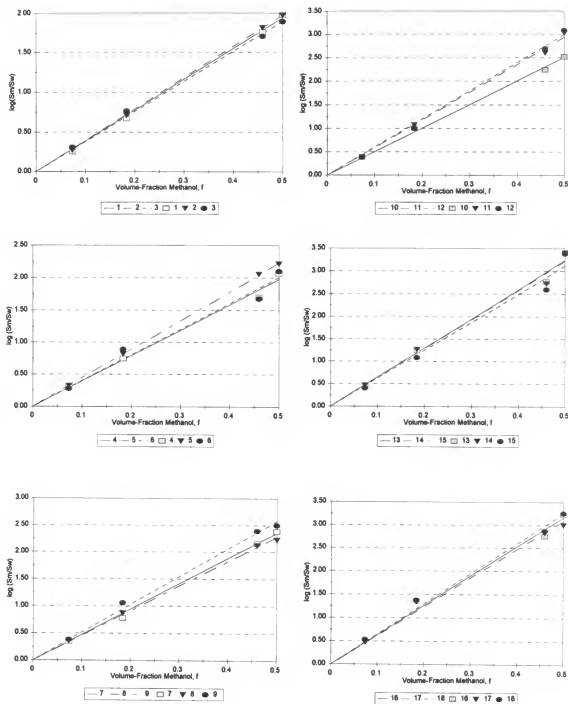


Figure 2-2. Measured solubilization profile of PAHs in methanol-water, ethanol-water, and MTBE-water mixtures. Solid and dashed lines represent the log-linear model.

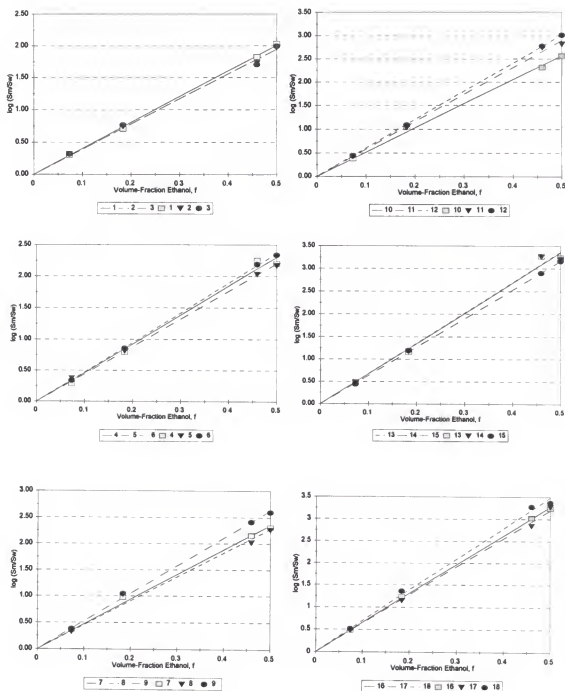


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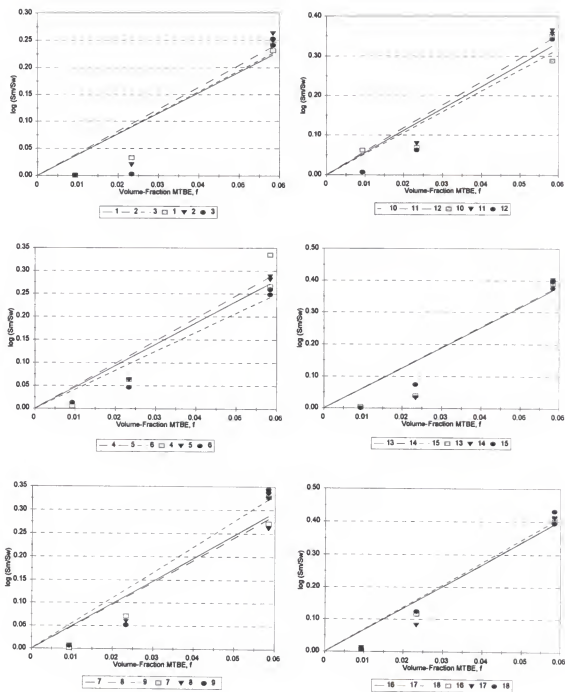


Figure 2-2. (Continued).

solute, the greater the solubility would be enhanced with an increase in the fraction of cosolvent. The PAH solubility increased essentially in a log-linear manner with the increasing volume fraction of methanol and ethanol. Deviations from log-linearity were observed within ± 0.5 log units.

The average calculated cosolvency powers (σ) of methanol, ethanol, and MTBE for eighteen PAHs are listed in Table 2-3. It is observed that σ values increase with increasing hydrophobicity of the solute for a given cosolvent. Previous researchers (Morris et al., 1988; Pinal et al., 1990) suggested that the cosolvency of completely miscible organic solvents (CMOSs) increased with decreasing solvent polarity. In this study, the same trend was observed. The cosolvency power of ethanol is larger than that of methanol for eighteen PAHs (where polarity of methanol = 6.6, and polarity of ethanol = 6.2, (Snyder, 1978)). The cosolvency power of MTBE is the highest in all three systems.

The average cosolvency power obtained from this study was compared with previous research (Morris et al., 1988; Pinal et al., 1990; Lane and Loehr, 1992). In general, the values for σ were typically larger than the earlier reported values. Several factors may have caused the deviations from the log-linear model, resulting in the higher magnitude of cosolvency powers in this study compared to those of previous investigators. When water-cosolvent interactions are significant, deviations are found from the log-linear solubility profiles predicted by eq (2-1). Deviations are quantified by the degree of nonideality of the solvent mixture. Such water-cosolvent interactions can be accounted for by the term β as described in eq (2-3). In this study, the values of β

Table 2-3 Cosolvency power of oxygenated compounds to PAHs.

Solutes	Cosolvents			Previous research	
	Methanol	Ethanol	MTBE ^a	Methanol	Ethanol
naphthalene	3.72	3.99	4.06	3.39 ^b , 3.42 ^c	3.48 ^b
2-methylnaphthalene	3.88	4.03	4.38	—	—
1-methylnaphthalene	3.97	4.05	4.22	—	—
acenaphthylene	4.06	4.27	4.44	—	—
acenaphthene	4.44	4.58	4.88	3.59 ^d	—
fluorene	4.12	4.68	4.35	3.62 ^d	—
phenanthrene	4.61	4.89	5.13	3.31 ^b , 4.24 ^d	—
anthracene	4.67	4.75	5.03	4.21 ^b , 4.06 ^c	4.29 ^b
fluoranthene	5.31	5.34	5.84	4.73 ^c , 4.65 ^d	—
pyrene	5.19	5.29	5.46	4.30 ^b , 4.93 ^c 4.69 ^d	—
benzo(a)anthracene	5.74	5.80	6.16	5.22 ^d	—
chrysene	5.68	6.00	5.86	4.96 ^b , 4.40 ^d	—
benzo[b]fluoranthene	6.44	6.65	6.75	6.53 ^d	—
benzo[k]fluoranthene	6.51	6.60	6.84	—	—
benzo[a]pyrene	5.95	6.29	6.63	4.05 ^d	—
indeno[1,2,3-cd]pyrene	6.66	6.61	6.95	—	—
dibenzo[a,h]anthracene	6.50	6.40	7.06	—	—
benzo[ghi]perylene	6.90	7.08	7.09	—	—

a. Based on volume fraction 0.058 only.

b. From Morris et al., 1988.

c. From Pinal et al., 1990.

d. From Lane and Loehr, 1992.

varied from 0.99 to 1.47 and 1.11 to 1.15 for methanol and ethanol, respectively. This is consistent with the results of previous investigators (Fu and Luthy, 1986a; Pinal et al., 1990).

Deviation from the log-linear model may also have resulted from cosolvent-sorbent interactions. Since sorption is inversely related to solubility, sorption decreases logarithmically with increasing cosolvent fraction as described in eq (2-9). The facilitated solubilization of PAHs from the coal tar phase into the aqueous phase indeed is the desorption of PAHs from sediment phase into aqueous phase. The variation in the solubilization effects of the cosolvents, as reflected in the range of α values, has been attributed to solvent-sorbent interactions. In the cosolvent system, for complex mixtures such as coal tar or soil contaminated with PAHs, the presence of a high loading of multiple components will affect the equilibrium concentration over time due to changes in mole fraction. A decrease in the mole fraction of all PAH constituents occurs when the cosolvent partitions into the coal tar phase, and at high cosolvent fractions the mole fraction can also change when significant amounts of the PAHs are extracted from the complex mixture.

The third factor affecting the magnitude of the cosolvency power is the contribution of PAHs to the aqueous phase caused by fuel constituents (the partitioning of PAHs from oxygenated fuel into the cosolvent/water mixture in the initial stage of spill). The batch equilibration experiment design allowed partitioning of PAH constituents of fuel into cosolvent/water. The partitioning of PAHs into the cosolvent/water phase is greater compared to the partitioning of PAHs into water alone (due to the introduction of

oxygenated compounds). With the partition of PAHs from fuel constituents into the cosolvent/water phase, the aqueous concentrations of PAHs will increase more than expected. Thus, the PAH concentrations that were measured includes PAHs from coal tar as well as from the fuel constituents. A compound such as naphthalene from the fuel will have a significant effect on aqueous concentrations because of its abundance in unleaded gasoline (0.2 to 0.5 % by volume (Cline et al., 1991)). Therefore, more naphthalene will tend to dissolve in the cosolvent/water phase compared to the pure aqueous phase. However, for benzo(b)fluoranthene and anthracene such an effect is less significant because these components are very minor constituents in oxygenated fuel formulations.

The solubility enhancement of PAHs by MTBE is not obvious (Figure 2-2), because of the low volume fraction of MTBE present in the aqueous phase. This is due to the relatively low miscibility of MTBE in water compared to methanol and ethanol. Analytical difficulties will increase for concentrations of PAHs with higher hydrophobicity in low volume fractions of cosolvent (less than 5%). After the dilution effect, such a solubility increase was difficult to measure and would not be significant at the field scale. Thus, the calculation of the average cosolvency power of MTBE (Table 2-3) did not include those values from the volume fractions of MTBE at 0.009 and 0.0234 but rather included only the volume fraction of 0.058.

Correlation Between Cosolvency Power And log K_{ow}

The equation governing the relationship between cosolvency power ($\alpha\beta\sigma$) and log K_{ow} (Eq 2-5) suggests that, if a given cosolvency power can be experimentally determined

for HOCs where K_{ow} 's are known, then the values of the slope and intercept can be determined. The relationships of cosolvency power versus $\log K_{ow}$ of PAHs in the methanol-water, ethanol-water, and MTBE-water systems are shown in Figure 2-3. The numbers in Figure 2-3 correspond to the compounds listed in Table 2-1.

For most of the PAHs in methanol-water and ethanol-water systems, the experimental values fall within an acceptance range of a factor of two (dashed line). A reasonable agreement was observed between measured cosolvency power and regression values (solid line). Observed deviations from the linear relation could be the result of various experimental artifacts, including possibly inadequate equilibration time and reduced recovery of the PAHs from the aqueous phase. This mainly results from the low solubility of the higher molecular weight PAHs where great difficulties are often encountered in accurately measuring the aqueous concentration, even with the solubility enhancement of a cosolvent. Also, cosolvent-water interaction is likely to be another factor to contribute such deviations. The MTBE-water system has the highest variability which may be due to the low volume fraction of MTBE present in the binary system. An acceptance range of a factor of four (short dashed line) was set to indicate such variability. It was found that for a partially-miscible organic solvent (PMOS) to significantly affect the solubility of an HOC, it is required that the PMOS volume fraction be the order of 1% or higher (Pinal et al., 1990). For MTBE, due to its limited aqueous solubility, the cosolvent effect was seen only at the simulated spill site which had the highest volume fraction of cosolvent at 0.058. With the subsequent dilution effect of river water, this cosolvent effect may be no longer significant at volume fractions 0.009

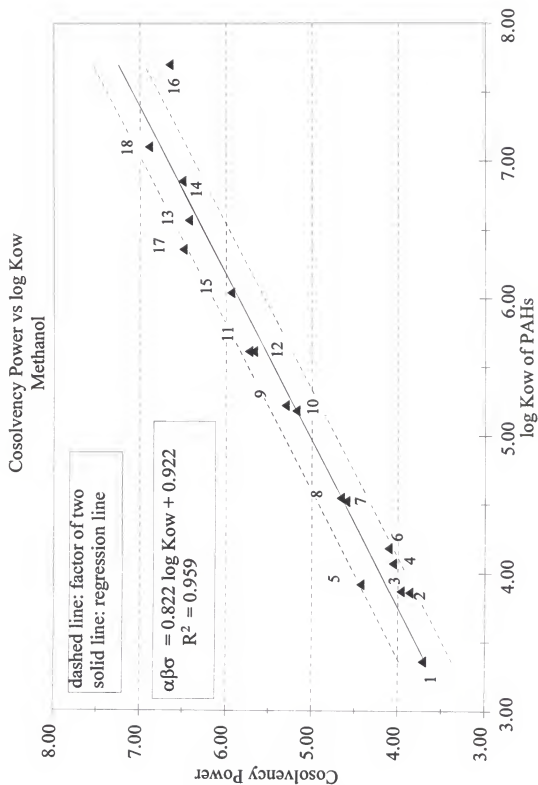


Figure 2-3. Cosolvency powers of methanol, ethanol, and MTBE versus log K_{ow} for 18 PAH compounds.

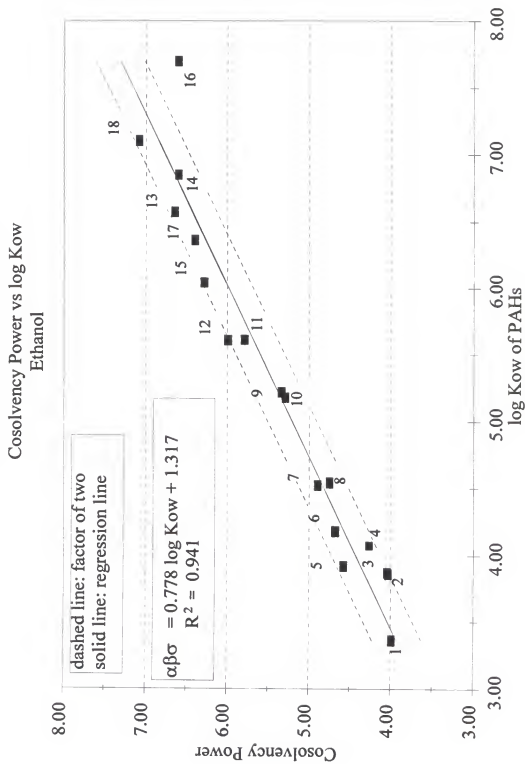


Figure 2-3. (Continued).

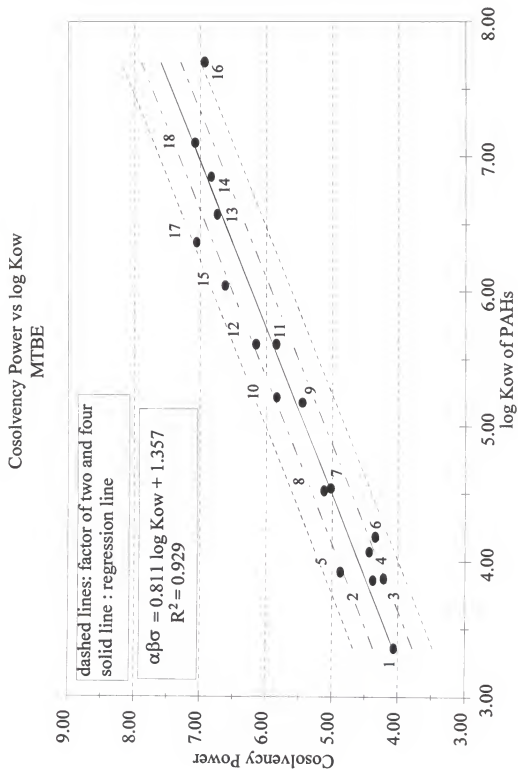


Figure 2-3. (Continued).

and 0.023, which contrasts with the finding of Pinal, et al., 1990. The high degree of correlation (R^2 ranged from 0.929 to 0.959) over several orders of magnitude of K_{ow} makes these empirical equations useful to predict the cosolvency power of oxygenated compounds (e.g., methanol, ethanol, and MTBE) for PAH compounds where the K_{ow} of a compound is known.

Conclusions

The alternative fuels (M-85 and E-85) used in this study are not now commercially available. However, these fuels might be used in the near future depending on a change in U.S. energy policy. The use of oxygenated fuels has received much attention in recent years as a way to minimize combustion-related pollution. The environmental impact of a probable fuel spill can be estimated from knowledge of environmental organic chemistry and the reactivity of fuel constituents in the aquatic system. The scenarios addressed here emphasize the significance of "secondary contamination" in an aquatic system due to a high alcohol content in fuel when an oxygenated fuel spill occurs. As mentioned in the Introduction section, this will be a potential problem when alternative fuels become widely used.

Based on this study, the solubility of PAHs in the aqueous phase is expected to increase due to the presence of methanol and ethanol when an oxygenated fuel spill occurs. Even with the simulated dilution effect in an aquatic system, methanol and ethanol still demonstrate cosolvent tendencies to facilitate solubilization of the hydrophobic PAHs from contaminated sediment. The results indicate that PAH solubility

increased essentially in a log-linear manner with an increased volume fraction of methanol and ethanol. Deviations from a log-linear relationship were observed for MTBE due to its limited aqueous solubility, and the cosolvent effect was seen only at the simulated spill site. A linear relationship between the logarithm of octanol/water partition coefficient and cosolvency power was observed for 18 PAH compounds.

It should be noted that the cosolvent effect will occur at various volume fractions of cosolvent, and not just occur at high volume fraction. However, at a low volume fraction of cosolvent, solubility enhancement will be difficult to determine for hydrophobic organic compounds (e.g., PAHs or PCBs) due to analytical constraints. Therefore, in the experimental design, the "worst case scenario" was simulated. The design of the batch dilution experiment in this study tended to represent a major spill in a river. Thus, a high fuel/water ratio (1:1 in volume) was selected to represent the spill site. The dilution effect for a real spill depends on the amount of fuel and flow rate of a river. Thus, it may vary depending on the hydrodynamic parameters. In order to allow the cosolvent (cosolubility) effect to occur, certain volume percentages of cosolvent are required in the system. Therefore, the dilution experiment represented a wide spectrum of volume fractions of cosolvent under certain dilution effects of water (i.e., 0.459, 0.184, and 0.0735 for methanol and ethanol).

This study provides a basis to predict the facilitated transport of PAHs from coal tar contaminated sediment due to the cosolvent effects of an oxygenated fuel spill. The information allows further assessment of the environmental and health effects of spills and leaks of oxygenated fuels.

CHAPTER 3

ENHANCED MOBILIZATION OF POLYNUCLEAR AROMATIC HYDROCARBONS BY COLLOIDS DUE TO THE COSOLVENT EFFECT OF OXYGENATED FUELS

Introduction

Field and laboratory evidence has established that partitioning/association of HOCs with colloids or very small particles must be considered in many groundwater and aquatic systems to account for the observed distributions of HOCs in the dissolved and particulate fractions of water samples (e.g., Gschwend and Wu, 1985; Baker et al., 1986). Equilibrium speciation of HOCs should include three phases: (a) the dissolved phase; (b) HOCs sorbed to non-settling particles or macromolecules (colloids); and (c) HOCs sorbed to settling solids (Gschwend and Wu, 1985; McDowell-Boyer et al., 1985; Enfield et al., 1989; Pankow and McKenzie, 1991).

Colloids range from a few nanometers to about a few micrometers in diameter (Stumm, 1977). Colloids have large surface area to volume ratios as the particulate phase, and non-existent settling rates which similar to the dissolved phase. Colloidal organic matter may sorb nonpolar organic chemicals much like organic materials associated with larger soil and sediment particles (McCarthy and Zachara, 1989; Schwarzenbach et al., 1993). The accumulation of HOCs at a colloidal interface is reversible; thus, sorbed contaminants may be released into solution as the particles are carried from one environment to another. Uptake of colloids by aquatic biota is

accompanied by coagulation or re-dispersion and occurs as a result of changes in adsorption equilibrium.

The fundamental process which controls the fate and transport of HOCs in aquatic and terrestrial environments is the distribution of these compounds between dissolved and sorbed phases. Colloids serve an important role in the release of HOCs from sediment to overlying water (Di Toro et al., 1982; Voice, et al., 1983; Gschwend and Wu, 1985; Baker et al., 1986; Chin and Gschwend, 1991; 1992). The association of HOCs with colloidal organic matter results in several important effects on the behavior of these compounds. First, HOCs behave differently in many ways when associated with colloids than they are dissolved in water. Second, colloidal binding of HOCs diminishes the tendency of HOCs to bioaccumulate in aquatic organisms. Third, the difficulties involving in separating the colloidal and dissolved phases of HOCs can impact the interpretation of data in distribution studies. Thus, sorption coefficients appear to decrease with greater loads of total solids (and colloids) in batch sorption systems (Schwarzenbach et al., 1993).

The cosolvent effect of oxygenated fuels on the solubility enhancement of hydrophobic organic compounds (HOCs) was addressed in the previous chapter. The effect can be summarized as follows: (1) the presence of the cosolvent in an oxygenated fuel (e.g., M85, which is 85% methanol and 15% gasoline) could enhance the transport of the gasoline constituents contained in the fuel when a fuel spill occurs. Thus, the potential for gasoline contamination will increase; (2) sorption will decrease in a log-linear manner upon addition of a cosolvent (Rao et al., 1985; Nkedi-Kizza et al., 1985; Fu and Luthy, 1986a); and (3) the addition of cosolvents has been shown to increase mass

transfer rates in sorption (Nkedi-Kizza et al., 1989; Brusseau et al., 1991; Augustijn et al., 1994). Therefore, the cosolvent-induced solubilization of HOCs coupled with colloid-bound HOCs into the aqueous phase becoming an important issue.

The objective of this study is to focus on the facilitated transport of polynuclear aromatic hydrocarbons (PAHs) in the colloidal phase by cosolvent effect of oxygenated fuels in a sediment/water system. Since PAHs are common HOCs in sediments that could be mobilized by a potential oxygenated fuel spill, coal tar contaminated sediment was selected as the source of the contaminated sediment. A quantitative assessment was made for distribution of PAHs into a three-phase system facilitated by the oxygenated compounds. The significance of the colloidal phase in a contaminated sediment/water system and the three-phase redistribution of PAHs upon the introduction of a cosolvent in a simulated river system was evaluated in this laboratory study.

Theory

The distribution of HOCs in aqueous systems is too complex to model as a linear, two-phase sorption equilibrium due to poorly defined phases and slow kinetics. Three phases are typically studied in surface water systems including: the mobile dissolved phase; a stationary particulate solid phase; and a mobile colloidal phase. The partitioning of HOCs between water and colloidal suspended solids is one of the most crucial processes, because it affects the further transfer of contaminants to the biotic compartment and ultimately to humans (Voice et al., 1983). Previous studies indicated that low concentrations of dissolved and/or suspended particulate-bound natural organic

matter in water can significantly enhance the solubility and stability of HOCs (Caron et al., 1985; Chiou et al., 1986; 1987; Schlautman and Morgan, 1993).

The redistribution and facilitated transport of HOCs by oxygenated fuels involves two processes. The first process involves increased solubility due to the cosolvent effect (Chapter 2). Such cosolvent-induced solubilization of HOCs into water will increase the potential for secondary contamination. Thus, HOCs will desorb from sediment or soil into the aqueous phase. The second process, dilution of the cosolvent, will occur as the mixture migrates away from a spill site. Therefore, the cosolvent effect will decrease and with log-linearly decreasing solubility with decreasing cosolvent content, the HOCs may possibly condense onto colloidal particles. Colloids therefore can act as nucleating agents for condensing HOCs as the cosolvent fraction decreases and will travel with water flow and cause much greater dispersion of HOCs than is otherwise expected. These processes are illustrated in Figure 3-1.

The PAH concentration in the liquid phase is subdivided into: (1) the concentration in the dissolved phase, and (2) the colloid associated phase. The experimentally observed concentration of PAHs in the aqueous phase is operationally defined. The observed aqueous concentration (C'_w) consists of a component in "true" solution (dissolved phase) and a component associated with colloidal particles (colloidal phase). The observed "apparent" aqueous concentration can be expressed as follows:

$$C'_w = C_w + C_{col} \quad (3-1)$$

where C_w is the true concentration of the PAH in water (mg/L of water); C_{col} is the

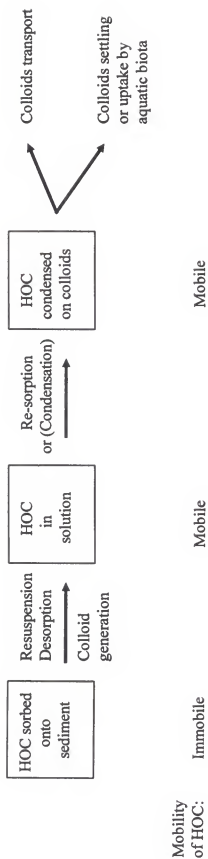


Figure 3-1. Cosolvent effect processes involving oxygenated fuels in the redistribution and facilitated transport of HOCs.

apparent concentration associated with colloids (mg/L of water), where $C_{col} = C_c * C_{col}^*$ and C_{col}^* is the concentration of colloids in water (kg colloid/L) and C_c is the PAH sorbed in colloids (mg/kg of colloid). The sorption coefficient between the colloidal and aqueous phases can be defined as

$$K_{col,w} = C_c / C_w \quad (3-2)$$

Combining eq (3-1) and (3-2),

$$C'_w = C_w (1 + K_{col,w} C_{col}^*) \quad (3-3)$$

With the spill of oxygenated fuels into a contaminated sediment/water system, the observed concentration of PAHs in the aqueous phase will be influenced by the cosolvent effect. A simple relationship describing the influence of cosolvent on the solubility of a solute in the mixed-solvent system is the log-linear cosolvency model (Yalkowsky et al., 1972; 1976; Yalkowsky and Rubino, 1985; Fu and Luthy, 1986b; Rao et al., 1991):

$$\log C_m = \log C_w + \beta \sigma f_c \quad (3-4)$$

where C is the observed aqueous concentration of the PAH in water (w) and mixed-solvent (m), f_c is the volume fraction of organic cosolvent in the aqueous phase, β is an empirical coefficient that accounts for water-cosolvent interactions, and σ represents the cosolvency power of the cosolvent.

For the sorption of PAHs from aqueous-organic binary solvent mixtures, the sorption coefficient is predicted to decrease exponentially as the fraction of organic solvent increases. A log-linear cosolvency model has been established to relate the equilibrium sorption coefficient (K_p) to the volume fraction of cosolvent from binary mixed solvent (Rao et al., 1985; 1990; Kimble and Chin, 1994) and is expressed as:

$$\log K_{p,b} = \log K_{p,w} - \alpha\beta\sigma f_c \quad (3-5)$$

where $K_{p,b}$ and $K_{p,w}$ are the equilibrium sorption constants for the binary solvent and aqueous systems, respectively, α is a nonideality coefficient that accounts for cosolvent-sorbent interactions, β is an empirical coefficient that accounts for water-cosolvent interactions, and σ is the cosolvency power of the cosolvent.

The addition of a cosolvent will result in a decrease in retardation and sorption coefficient (K_p) of HOC. Such phenomena have been demonstrated by many researchers (Fu and Luthy, 1986b; Nkedi-Kizza et al., 1985; 1987; 1989). With the potential spill of oxygenated fuels into a contaminated sediment/water system, the observed aqueous concentration of PAHs in aqueous phase will be the result of the cosolvent effect. The cosolvent effect can occur in two ways. First, the facilitated solubilization of PAHs (C_w) will follow the log-linear model as described in eq (3-4). Second, the sorption coefficient ($K_{col,m}$) of HOC onto colloids will decrease exponentially as the volume fraction of cosolvent increases following eq (3-6):

$$\log K_{col,m} = \log K_{col,w} - \alpha\beta\sigma f_c \quad (3-6)$$

$$K_{col,m} = K_{col,w} 10^{-\alpha\beta\sigma f_c} \quad (3-7)$$

where $K_{col,m}$ and $K_{col,w}$ are sorption coefficients for the binary solvent and aqueous systems, respectively. Due to the solubility enhancement in aqueous phase and sorption constraints in the colloidal phase, the apparent aqueous concentration ($C'_{w,m}$) becomes the following,

$$C'_{w,m} = C_{w,m} + C_{col,m} \quad (3-8)$$

where $C'_{w,m}$ is the “apparent” aqueous concentration in water/solvent mixture, $C_{w,m}$ is the true concentration of the PAH in water/solvent mixtures (mg/L of mixture); $C_{col,m}$ is the apparent concentration associated with colloids under the influence of cosolvent (mg/L of mixture); $C^*_{col,m}$ is the concentration of colloids in binary mixture (kg colloid/L), and $C^*_{col,m} \cong C^*_{col}$. Thus, similar combination as eq (3-3) will be derived,

$$C'_{w,m} = C_{w,m} (1 + C^*_{col,m} K_{col,m}) \quad (3-9)$$

Substituting the expression for $K_{col,m}$ from eq (3-7) into eq (3-9) gives

$$C'_{w,m} = C_{w,m} (1 + C^*_{col,m} K_{col,w} 10^{-\alpha \beta \phi}) \quad (3-10)$$

To quantify the colloid effect on the observed aqueous concentration of PAHs, the magnitude of colloids effect is represented by ϕ ,

$$\phi = C^*_{col,m} K_{col,w} 10^{-\alpha \beta \phi} \quad (3-11)$$

where all the terms were defined earlier.

Materials and Methods

Coal tar contaminated sediment from Harbor Point, New York was used to study the redistribution of polynuclear aromatic hydrocarbons (PAHs) in the sediment, colloidal, and aqueous phases in a simulated spill into a river system. The organic carbon content of the contaminated sediment was determined to be 5.62%. Eighteen target PAHs were of interest in this study (Table 2-1) and this numbering sequence is used throughout this chapter. The total PAH content (sum of eighteen PAHs) in the coal tar contaminated sediment was approximately 800 mg/kg. The oxygenated compounds used in the study were (Chapter 2): methanol, ethanol, and MTBE.

Dilution Effect Experiment

The partitioning behavior of multi-component liquids in water has been addressed by several studies that employed the Raoult's law convention for activity coefficient calculations in conjunction with liquid or supercooled liquid solubilities to estimate aqueous-phase concentrations of aromatic hydrocarbons (Cline et al., 1991; Lee, et al., 1992a; 1992b; Chen, et al., 1994; Peters and Luthy, 1993; 1994). The Raoult's law-based approach can be adopted to evaluate the redistribution of PAHs in different phases due to the cosolvent effect of oxygenated fuels.

Potential spills of oxygenated fuels in surface water/sediment system were simulated in the laboratory. Equilibrium concentrations of PAHs in sediment/water systems were determined in a sequential batch dilution experiment. This experimental design represents the dilution effect in a river system in which an oxygenated fuel spill has occurred. A fuel/water ratios of 1:1 (representing the spill site) was used in the batch equilibration experiments. Two hundred grams of contaminated sediment, 800 mL of alternative fuel, and 800 mL of deionized (D.I.) water were placed in a 2-L reaction bottle which was equipped with a ground glass stopper and a Teflon® stopcock positioned approximately two inches from the bottom. Each reaction bottle was agitated by horizontal shaking on a shaker tray at room temperature ($22\pm2^{\circ}\text{C}$) for 2 hours. After shaking and a quiescent period of 20 minutes, the three phases (fuel, aqueous, and sediment) were collected separately from each reaction bottle. A volume of 480 mL of water was subsampled for analysis. A second aqueous sample (320 mL) was placed in a clean reaction bottle containing 480 mL of fresh D.I. water and 200 g of contaminated sediment. The resulting mixture was agitated again for 2 hours. Then, 480 mL of water

was taken for analysis and the remaining 320 mL went to the next reaction bottle. These water/sediment equilibrations were conducted twice to allow water (which contains the oxygenated compound) from the spill site to contact new sediment, representing the dilution of cosolvent in a river system. Each experiment was run in triplicate. A control experiment (sediment/water) was also conducted by using the same procedures to evaluate colloidal phase concentration of PAH under the circumstance of no cosolvent present.

The redistribution of contaminants (PAHs) into different phases by cosolvent-induced solubility enhancement was evaluated. The advantage of this experimental design is that the mass balance of PAHs can be readily established. To generate the similar concentration levels of colloids in all experiments, a preliminary experiment was conducted to measure the total suspended solids in various fuel/water/sediment systems. The total suspended solid concentration was found to be about 7 mg/L in all the systems.

Additional experiments were conducted to serve as a basis for comparison when evaluating the cosolvent effect of oxygenated compounds in the absence of fuel components. The aqueous concentration of PAHs in binary solvent mixtures (i.e., methanol/water or ethanol/water) was determined. Instead of using oxygenated fuels, an individual oxygenate compound (e.g., methanol) was used separately to equilibrate with contaminated sediment/water system. The experimental protocol followed the same volume ratio (1:1 oxygenate/water), equilibration time, and sample analysis as did the previous experiments.

PAH Analysis

Sediment samples from the dilution experiment were extracted using a batch extraction method (Chen et al., 1996). Approximately 5 g of coal tar contaminated sediments were placed in 50-mL Kimax tubes, and sequentially extracted with 1:1 v/v methanol/methylene chloride. Six replicates were performed. The first extraction step involved equilibration of sediment for 24 hr with 25 mL of the solvent mixture on a rotary shaker. Two sequential extractions involved equilibrations with 10 mL of solvent mixture. After each extraction step, the soil was centrifuged for 30 min. The supernatant was passed through a 0.20 μm Teflon[®] filter followed by a sodium sulfate column to remove residual water and was then stored in a vial with a Teflon[®] lined septum at 4°C.

The aqueous samples from the same experiments were divided to two subsamples, one treated with ultrafiltration and the other untreated, to differentiate PAHs in the colloidal phase. Prior to ultrafiltration, aqueous samples were filtered through a Teflon[®] filter (0.45 μm). Ultrafiltration was chosen to isolate colloids because it is nondestructive. A stirred cell Ultrafiltration Unit (Amicon, Beverly, MA) was used by employing a ultrafilter membrane. The membrane on a ultrafilter with molecular weight cut off (MWCO) lower than 3,000 does not stand for solution with more than 10 % of alcohol. Thus, the ultrafilter with MWCO equal to 3,000 was selected in this study. Nitrogen (55 psi) was applied to the ultrafiltration cell unit during filtration. The filtrate was collected in a flask and stored at 4°C until extraction.

The aqueous samples were extracted three times with methylene chloride, followed by rotary evaporation, and then the extracts were passed through a sodium sulfate column to remove residual water. The extract volume was further reduced to 1 mL by a gentle

flow of nitrogen gas. The extracts were transferred to 1 mL crimp-seal vials with Teflon® lined septum and stored refrigerated (4°C) until analysis.

The sediment and aqueous extracts were analyzed using a Perkin-Elmer 8500 gas chromatograph/ion trap detector (GC/ITD) equipped with a Perkin Elmer AS 8300 autosampler. The GC column was a 0.25 mm i.d., 30 meter, fused silica XTI-5 (5% diphenyl-95% dimethyl polysiloxane) column with a 0.5 µm film thickness (Restek Corp). The temperature program consisted of a 4 min hold time at 60°C, a ramp to 120°C at 7°C/min followed by a second ramp to 270°C at 10°C/min, and a final ramp to 300°C at 30°C/min followed by a 17 min hold time (Chen et al., 1996). Both injector and detector temperatures were maintained at 250°C. Internal standard calibration was performed during GC/ITD analyses.

Results and Discussion

Colloids have been suggested to be able to bind and stabilize PAHs in natural waters (Means and Wijayaratne, 1982; Chin and Gschwend, 1992). The magnitude of this binding phenomenon appears to be dependent on the nature of colloids (i.e., organic carbon content). To quantify the magnitude of colloid-bound PAHs, the aqueous samples were divided into two sets of subsamples as described previously. The first set of subsamples was subjected to ultrafiltration to remove colloids before PAH analysis. One basic assumption should be made is all colloids will be retained by ultrafilter. Thus, subtraction of permeate from original sample will be the retented colloids. Measurement of PAH concentrations in two subsamples (with or without colloids) in mixed solvent system are represented by the apparent ($C'_{w,m}$) and “true” aqueous concentration ($C_{w,m}$),

respectively. The relationship between two subsamples was described by eq (3-9) in the Theory section. Due to the cosolvent effect of oxygenated fuels, the aqueous concentrations of PAHs increased by several orders of magnitude. Solubility enhancement of PAHs was characterized by cosolvency power (σ) using eq (3-4).

The concentrations of PAHs in the colloidal and true aqueous phases after equilibration with M85, E85, and oxygenated gasoline are shown in Tables 3-1 to 3-3, respectively. It was found that both the "apparent" and "true" aqueous concentrations of PAHs in the various binary cosolvent-water mixtures showed a reasonable log-linear relationship according to eq (3-4). These results suggest that the more hydrophobic the HOCs, the greater is the solubility enhancement with an increase in the fraction of cosolvent. The experimental design allowed various volume fractions of cosolvent to be introduced into the sediment/water systems (creating the dilution effect). Thus, calculation of cosolvency power was based on results of different volume fractions of cosolvent present in the system (e.g., the volume fraction of methanol was 45.9%, 18.4%, and 7.4% in dilution effect experiment, respectively). The average cosolvency powers (σ) of methanol, ethanol, and MTBE are listed in Table 3-4.

If the colloidal effect was neglected from the aqueous phase, which means measurement of solubility enhancement using true aqueous concentration ($C_{w,m}$), the cosolvency power obtained here shows similar results as those obtained from earlier research (Chen and Delfino, 1996). The PAH solubility increases essentially in a log-linear manner with an increasing volume fraction of methanol and ethanol. Deviations from log-linearity were contained within ± 0.5 log unit. It was found the cosolvency

Table 3-2. The colloidal and true aqueous phase concentrations of PAHs after equilibration with E85.

Volume fraction (f) Sample	Colloidal phase concentration (mg/L)				True aqueous phase concentration (mg/L)			
	E-85/water/seed				E-85/water/seed			
	EtOH/water/seed	0.459	E-1	0.184	0.074	EtOH/water/seed	0.459	E-1
	E-0			E-2	E-3	E-0		E-2
NAPHTHALENE	9.37E-01	1.02E+00	5.76E-02	2.88E-02	4.25E+00	2.51E+00	3.25E-01	1.44E-01
2-METHYLNAPHTHALENE	8.58E-02	9.88E-02	9.96E-03	1.84E-03	4.85E-01	3.38E-01	3.20E-02	1.12E-02
1-METHYLNAPHTHALENE	1.94E-01	2.18E-01	1.33E-02	2.47E-03	7.31E-01	5.40E-01	3.03E-02	8.55E-03
ACENAPHTHYLENE	1.10E-02	1.30E-02	6.20E-04	2.50E-04	4.30E-02	2.97E-02	2.43E-03	7.10E-04
ACENAPHTHENE	9.37E-02	8.98E-02	1.19E-02	4.85E-03	7.45E-01	5.55E-01	5.23E-02	2.14E-02
FLUORENE	1.67E-01	2.15E-01	7.24E-03	2.83E-03	4.85E-01	3.98E-01	2.70E-02	1.03E-02
PHENANTHRENE	1.83E-01	1.93E-01	1.40E-02	2.15E-03	7.44E-01	5.78E-01	4.15E-02	1.21E-02
ANTHRACENE	1.53E-01	1.15E-01	1.03E-02	1.74E-03	4.04E-01	4.29E-01	2.30E-02	7.92E-03
FLUORANTHENE	1.74E-01	8.56E-02	3.74E-03	8.20E-04	3.92E-01	3.25E-01	1.31E-02	5.51E-03
PYRENE	7.65E-02	9.48E-02	6.38E-03	1.01E-03	4.63E-01	3.40E-01	1.79E-02	4.83E-03
BENZO(a)ANTHRACENE	5.00E-02	2.40E-02	7.37E-04	1.77E-04	8.89E-02	8.23E-02	2.10E-03	5.20E-04
CHRYSENE	2.74E-02	1.04E-02	2.07E-04	5.17E-05	6.09E-02	3.01E-02	8.53E-04	1.77E-04
BENZO(b)FLUORANTHENE	1.07E-02	8.22E-03	1.49E-04	2.77E-05	3.08E-02	2.10E-02	5.67E-04	4.00E-05
BENZO(k)FLUORANTHENE	1.04E-02	9.27E-03	3.15E-04	3.23E-05	2.94E-02	2.22E-02	3.60E-04	5.27E-05
BENZO(a)PYRENE	2.66E-02	1.62E-02	8.67E-04	7.16E-05	7.11E-02	3.09E-02	1.09E-03	1.47E-04
INDENO(1,2,3-cd)PYRENE	1.45E-02	6.46E-03	2.38E-04	3.77E-05	3.42E-02	1.76E-02	4.15E-04	1.05E-04
DIBENZO(a,h)ANTHRACENE	1.22E-02	6.55E-03	4.43E-04	5.03E-05	3.28E-02	1.81E-02	4.87E-04	1.20E-04
BENZO(ghi)PERYLENE	1.07E-02	1.07E-02	2.28E-04	2.30E-05	2.75E-02	1.75E-02	3.65E-04	5.40E-05
TOTAL PAH	2.24	2.23	0.14	0.05	9.12	6.28	0.57	0.23

Table 3-3. The colloidal and true aqueous phase concentrations of PAHs after equilibration with oxygenated gasoline.

Volume fraction (f) Sample	Colloidal phase concentration (mg/L)			True aqueous phase concentration (mg/L)		
	oxygenated gasoline/water/sed			oxygenated gasoline/water/sed		
	MTBE/water/sed	OG-0	OG-1	MTBE/water/sed	OG-0	OG-1
NAPHTHALENE	0.058	0.023	0.009	0.058	0.023	0.009
2-METHYLNAPHTHALENE	4.87E-02	4.83E-02	1.87E-02	1.11E-01	8.70E-02	7.00E-02
1-METHYLNAPHTHALENE	2.75E-03	2.88E-03	1.63E-03	1.10E-02	9.29E-03	5.79E-03
ACENAPHTHYLENE	5.04E-03	4.87E-03	2.14E-03	7.65E-03	6.60E-03	5.89E-03
ACENAPHTHENE	5.19E-04	5.60E-04	1.20E-04	7.53E-04	4.63E-04	3.74E-04
FLUORENE	6.45E-03	5.62E-03	3.72E-03	2.01E-02	1.32E-02	8.25E-03
PHENANTHRENE	4.70E-03	3.30E-03	3.70E-03	8.47E-03	5.70E-03	3.50E-03
ANTHRACENE	5.96E-03	7.07E-03	2.41E-03	1.43E-02	9.50E-03	8.43E-03
FLUORANTHENE	3.97E-03	4.70E-03	2.45E-03	1.17E-02	6.55E-03	7.92E-03
PYRENE	3.32E-03	2.20E-03	9.55E-04	4.55E-03	5.08E-03	1.84E-03
BENZO(a)ANTHRACENE	1.59E-03	1.10E-03	5.76E-04	4.64E-03	2.98E-03	2.75E-03
CHRYSENE	2.71E-04	2.45E-04	6.53E-05	4.56E-04	2.10E-04	2.13E-04
BENZO(b)FLUORANTHENE	1.20E-04	8.03E-05	2.89E-05	2.09E-04	1.56E-04	7.25E-05
BENZO(k)FLUORANTHENE	2.66E-05	1.60E-05	8.33E-06	4.97E-05	3.33E-05	1.62E-05
BENZO(a)PYRENE	4.37E-05	2.78E-05	4.10E-06	4.70E-05	4.55E-05	1.97E-05
INDENO(1,2,3-cd)PYRENE	1.38E-04	8.33E-05	2.33E-05	1.99E-04	1.60E-04	5.03E-05
DIBENZO(a,h)ANTHRACENE	5.88E-05	4.30E-05	6.00E-06	6.76E-05	5.73E-05	5.87E-05
BENZO(g,h,i)PERYLENE	3.93E-05	2.89E-05	9.63E-06	5.10E-05	4.33E-05	1.64E-05
TOTAL PAH	4.57E-05	2.89E-05	5.03E-06	5.30E-05	3.47E-05	1.90E-05
	0.08	0.08	0.04	0.20	0.19	0.14
			0.04			0.12

Table 3-4 The average cosolvency powers (σ) of oxygenated compounds in various fuel-water-sediment systems.

	Methanol	Ethanol	MTBE
naphthalene	3.38	3.61	3.80
2-methylnaphthalene	3.71	3.81	3.87
1-methylnaphthalene	4.16	3.93	4.63
acenaphthylene	4.10	4.31	3.91
acenaphthene	4.00	4.07	5.61
fluorene	4.28	3.93	5.99
phenanthrene	4.50	4.16	4.52
anthracene	4.30	3.81	6.78
fluoranthene	4.76	4.71	5.56
pyrene	4.53	4.52	4.68
benzo(a)anthracene	5.87	5.45	6.32
chrysene	5.87	5.72	6.76
benzo[b]fluoranthene	5.95	6.48	7.80
benzo[k]fluoranthene	6.27	6.08	6.33
benzo[a]pyrene	6.30	6.29	8.54
indeno[1,2,3-cd]pyrene	6.00	6.55	7.44
dibenzo[a,h]anthracene	5.96	6.41	8.29
benzo[ghi]perylene	6.44	6.57	7.99

power of completely miscible organic solvents increases with decreasing solvent polarity. Despite the complex nature of coal tar contaminated sediment, the cosolvency powers observed in this study showing a difference of less than 10 % with the previous study (Chen and Delfino, 1996).

The solubility enhancement of PAH by oxygenated gasoline is not obvious as related to the partially miscible nature of MTBE in aqueous phase. Meanwhile, analytical difficulties increase for PAHs that have higher hydrophobicity in a low volume fraction of cosolvent (less than 5%). After dilution effect in these experiments, such an increase was difficult to measure and would likely not be significant in a field scale application. Thus, the calculation of the average cosolvency power of MTBE did not include those values from the volume fraction of MTBE (0.94%).

Several factors may have caused the deviations from the log-linear model, resulting in the higher magnitude of cosolvency powers in this study compared to those of previous investigators (Morris et al., 1988; Pinal et al., 1990). Deviations from the log-linear cosolvency model were attributed to (1) water-cosolvent interactions, (2) cosolvent-sorbent interaction, and (3) fuel constituent-cosolvent interactions.

The cosolvency power of oxygenated compounds toward PAHs was larger than aqueous samples contained colloids. This is due to the contribution of colloid-bound PAHs in the aqueous phase. For all the PAHs selected in this study, the fraction in the colloidal phase in different fuel/sediment systems ranged from 18 to 46 % of the apparent aqueous phase concentrations (Table 3-5). It is noted that the fraction of colloid-bound PAH increases with the compound's hydrophobicity. Given the relationship described in eq (3-9), more hydrophobic compound will have larger $K_{col,m}$, therefore, the magnitude of

Table 3-5 The fraction in percent of PAH bound to colloids in varied fuel-water-sediment systems.

	M-85/water	E-85/water	Oxygenated gasoline/water	Control sediment/water
naphthalene	26.7	19.7	30.8	27.5
2-methylnaphthalene	19.5	18.9	21.1	33.7
1-methylnaphthalene	18.0	25.7	39.3	32.8
acenaphthylene	24.2	24.3	42.7	34.4
acenaphthene	27.3	25.5	23.3	24.5
fluorene	26.7	25.8	32.5	33.0
phenanthrene	23.4	21.3	32.5	31.7
anthracene	23.5	24.4	26.8	38.2
fluoranthene	26.1	21.7	36.2	31.0
pyrene	28.9	19.9	22.8	39.4
benzo(a)anthracene	29.2	27.5	39.3	41.2
chrysene	32.9	24.7	35.3	40.0
benzo[b]fluoranthene	36.0	28.9	33.6	43.5
benzo[k]fluoranthene	33.6	35.1	43.1	48.8
benzo[a]pyrene	32.8	34.7	37.6	51.5
indeno[1,2,3-cd]pyrene	37.2	29.8	44.7	49.8
dibenzo[a,h]anthracene	33.0	32.8	41.8	46.2
benzo[ghi]perylene	36.6	33.6	45.9	45.3

the colloid effect (ϕ) will be expected higher. By examining the values of ϕ in same fuel/water system, no significant change was found in terms of volume fractions of cosolvent. The change of ϕ in different volume fractions of cosolvent was observed within 10%.

It was observed that the fraction colloid-bound PAH in E85/water system has slightly higher contribution to the apparent aqueous concentration of PAHs than M85/water system for thirteen compounds. Ethanol has slightly larger cosolvency power to PAHs than methanol. The $K_{col,m}$ in methanol/water system is expected to be higher than in ethanol/water system. Thus, the magnitude of colloid effect in methanol/water system is slightly higher than in ethanol/water system. In the oxygenated gasoline/water system, the magnitude of the colloid effect was the highest (21 to 46%). The ϕ in oxygenated gasoline/water system is expected to be smallest among three systems. Apparently $K_{col,m}$ in MTBE/water system does not decrease as predicted. It could be the partially-miscible nature of MTBE in aqueous phase (smaller volume fraction) limited the cosolvent effect on the colloids (the desorption of PAHs from colloidal phase). By extrapolation of the cosolvent concentration to zero, the role of colloids results in a higher magnitude of ϕ shown in the control set of experiment (25 to 52%). Eadie et al. (1990) discovered that 52% of benzo(a)pyrene was in the free dissolved phase, 40% was associated with particulate matter, and only 8% associated with colloids. Chin and Gschwend (1992) found that 44 to 52% of pyrene and 25% of phenanthrene were bound to colloids in Boston Harbor sediment porewater. It is clear that the fraction of colloid-

bound PAH will be site specific and depends on the nature of colloids and the HOC hydrophobicity.

According to the experimental design, the abundance of colloids in the various fuel/water/sediment systems was maintained at the similar concentration levels based on the measurement of total suspended solids. Thus, the abundance of colloids in all of the systems should be at the same order of magnitude in the various fuel-spill experiments. However, the magnitude of colloid effect was minimized due to small quantity of colloids generated from the experiments. It is reflected by total suspended solid measurement, which is about 7 mg/L in all of the systems.

The introduction of cosolvent to the simulated river system will mobilize the release of PAHs from sediment into the aqueous phase, allowing the desorption of PAHs to increase. The sorption of PAHs onto colloids was constrained by the cosolvent effect, therefore, the sorption coefficients ($K_{col,m}$) decreased. As a result, the sorption equilibrium condition changed. Such an effect decreases the amount of colloid-bound PAH in the manner described by eq (3-7). Hypothetically, the sorption coefficients of PAHs in the colloid/water ($K_{col,w}$) and sediment/water (K_{sw}) phases should be very close at the same order of magnitude because of the similar chemical properties. However, in the early stage of an oxygenated fuel spill (when the fuel/water ratio is high), PAHs will desorb from sediment into the aqueous phase, as governed by the cosolvent effect. As the contaminant plume migrates, coupled with the dilution of the oxygenated compounds, PAHs may condense onto colloidal particles again. This results in an increased sorption coefficient ($K_{col,m}$) in the colloid/water phases down stream compared to $K_{col,m}$ in the fuel spill site. Based on two counteracting effects, sorption constraints (desorption rate

increases) and condensation of PAHs into the colloidal phase, the magnitude of the mobilization of PAHs by colloid transport is not as high as it was shown in control experiment. It was concluded that the cosolvent had a more significant effect than the colloids in terms of PAH mobilization in the aqueous phase. Apparently, the cosolvent effect dominates the role of colloids in the phase redistribution of PAHs.

An empirical relationship between the sorption coefficients ($K_{col,w}$ and $K_{col,m}$) and the solute physicochemical parameter (K_{ow}) was established for all three fuel/water systems (Figures 3-2). In the M85/water and E85/water systems, $\log K_{col,w}$ and $\log K_{ow}$ are highly correlated than in the oxygenated gasoline/water system. Overall the $K_{col,m}$ (the sorption coefficient under the influence of cosolvent) is about one to two log unit smaller than $K_{col,w}$ for all of the PAHs in various cosolvent/water systems. This is likely due to the increase of desorption rate (sorption constraint) by cosolvent effect as described earlier. It should be noticed that the values of $K_{col,w}$ are based on calculations using eq (3-7), not by direct measurement. Under the influence of cosolvent, the partition coefficients between colloid and water phases tends to reach same order of magnitude for all eighteen PAH compounds.

The correlation relationship between the estimated sorption coefficients ($K_{col,w}$ and $K_{col,m}$) in colloid/water phase and the sediment/water partition coefficient (K_{sw}) was also established (Figure 3-3). For M85/water and E85/water systems, the estimated sorption coefficients in colloid/water phase are highly correlated to the sediment/water partition coefficients. However, in the oxygenated gasoline/water system, they were not highly correlated. The values of $K_{col,w}$ are one to two log units smaller than K_{sw} . In nature water system, such difference may not be as significant as the system under the influence of

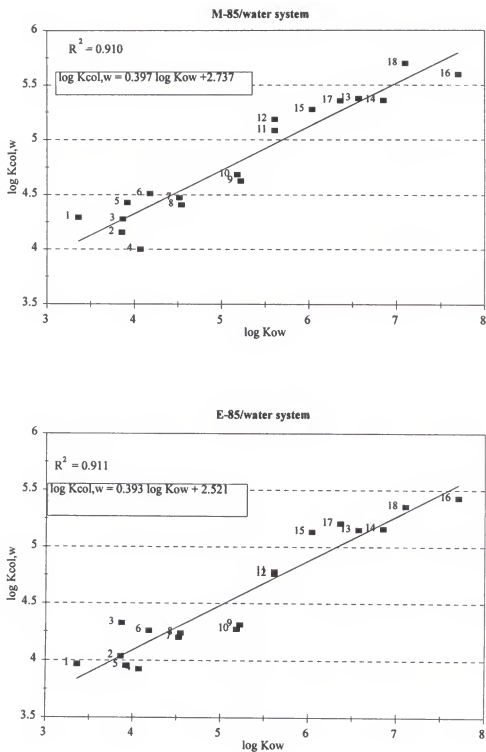


Figure 3-2. Logarithm of sorption coefficients of PAHs in colloid/water phase vs $\log K_{ow}$.

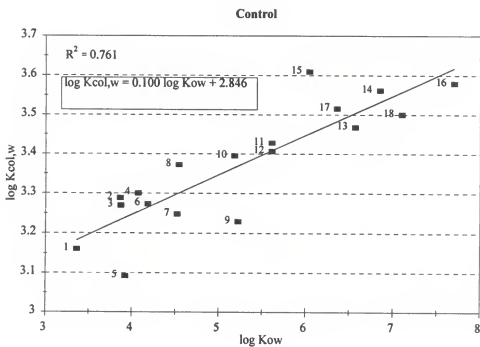
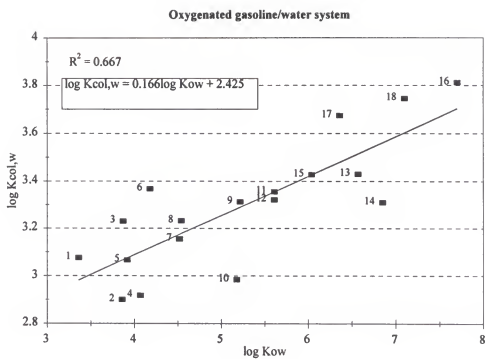


Figure 3-2. (Continued).

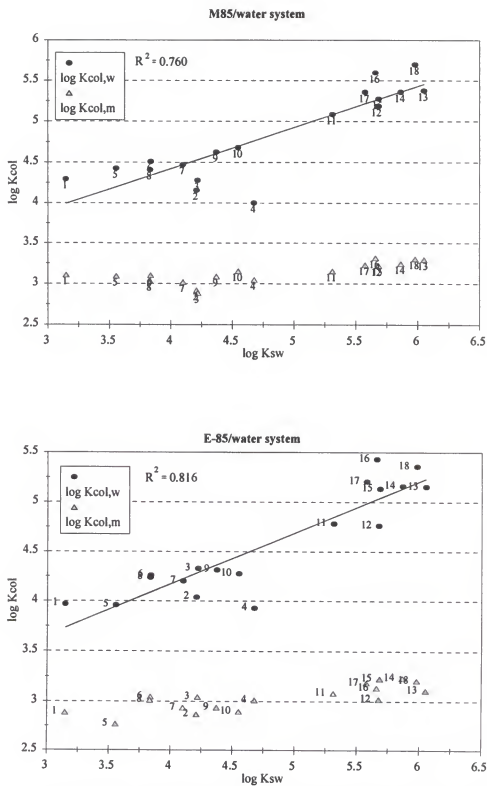


Figure 3-3. Correlation between the estimated sorption coefficients in colloid/water phase and the sediment/water partition coefficients.

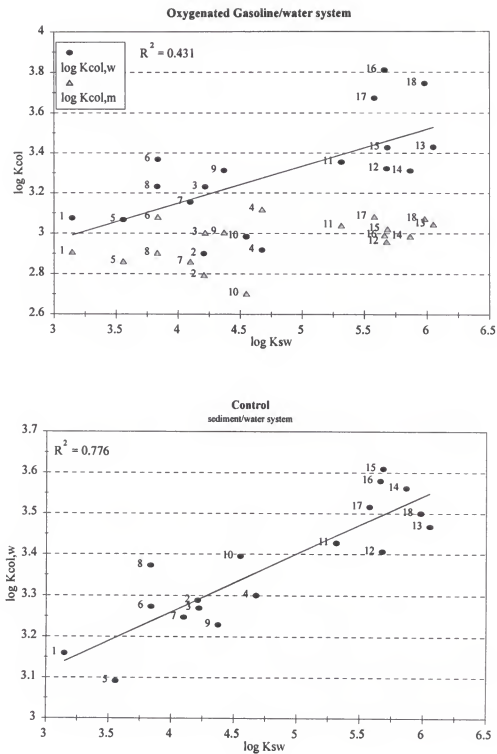


Figure 3-3. (Continued).

cosolvent (sorption constraint). Possible nonequilibrium sorption mechanisms are suspected to contribute to these results, such as the heterogeneous distribution of PAH constituents in sediment. Several analytical artifacts may contribute such derivation. First factor will be the incomplete phase separation due to the colloid-bound PAH break through ultrafilter (Burgess et al., 1996). Second, the sorption of colloids onto stir cell walls, which will result in an underestimated colloid/water partition coefficient. Third, analytical artifact arises for solubility measurement of high-hydrophobic PAHs in cosolvent mixtures.

Conclusions

The solubility of PAHs in the aqueous phase is increased by the presence of methanol and ethanol when an oxygenated fuel spill occurs. Even with the dilution effect in an aquatic system, the cosolvent effect still demonstrates a strong tendency to facilitate the solubilization of hydrophobic organic compounds from contaminated sediment. This study demonstrates the results of combining the cosolvent effect and with the contribution of the colloidal phase in the mobilization and redistribution of PAHs from contaminated sediment. These results will help to determine remediation strategies should an oxygenated fuel spill occur. This study also contributes to the understanding of the role of colloids in the release of PAHs from coal tar contaminated sediments to overlying waters when an oxygenated fuel spill occurs.

CHAPTER 4

COSOLVENT EFFECTS ON THE DISSOLUTION OF POLYNUCLEAR AROMATIC HYDROCARBONS DUE TO SPILLS OF OXYGENATED FUELS IN THE SUBSURFACE ENVIRONMENT

Introduction

The use of oxygenated fuels has brought increased interest in the transport and fate of miscible organic liquids in the environment and the effect that these liquids can have on the transport and fate of other contaminants (Squillace et al., 1996; Chen and Delfino, 1996). Oxygenated gasoline is currently used in several states under the mandate of the Clean Air Act Amendments of 1990. The 1990 Clean Air Act Amendments require fuel oxygenates, such as methyl tert-butyl ether (MTBE) or ethanol, to be added to gasoline in some metropolitan areas to reduce atmospheric concentrations of carbon monoxide and ozone. Also the oxygenated fuels have been studied by car manufacturers under the alternative fuel vehicle program for the purpose of reducing emissions. The alternative fuels, M85 and E85 (15% gasoline and 85% methanol or ethanol, respectively), were commonly selected to evaluate their performance under the original guidelines of the Alternative Motor Fuels Act of 1988 and the Energy Policy Act of 1992 (AFDC Update, 1996).

The addition of polar organic solvents that are completely-miscible or highly-soluble in water to a mixture of hydrocarbons and water has the potential of showing the cosolvent effect (Fu and Luthy, 1986a ; Munz and Roberts, 1986; Groves, 1988; Pinal et al., 1990).

Cosolvency is defined as the effect of organic solvents on the solubility and sorption of hydrophobic organic compounds (HOCs) (Rao et al., 1990). This can be described by the following observations: (1) water-miscible cosolvents such as ketones (e.g., acetone), and alcohols (e.g., methanol, ethanol) may reduce the net polarity of the oxygenate-water solvent. When a miscible constituent is added to water, it increases the quantity of nonionic organic compounds that can dissolve in the mixed solvent. For example, the presence of the cosolvent in an oxygenated fuel (e.g., M85, which is 85% methanol and 15% gasoline) could enhance the transport of the fuel constituents. Thus, the potential for fuel contamination will increase. Sorption will decrease in a log-linear manner upon addition of a cosolvent (Rao et al., 1985; Nkedi-Kizza et al., 1985; Fu and Luthy, 1986b). The addition of cosolvents has been shown to increase mass transfer rate in sorption (Nkedi-Kizza et al., 1989; Brusseau et al., 1991; Augustijn et al., 1994). Therefore, the use of oxygenated fuels indicates that cosolvency could be a very important phenomenon in the release and transport of contaminants that are present in soils.

The leak or spill of oxygenated fuel will induce a solvent flushing effect in the contaminated soil due to the high content of oxygenated compounds. The oxygenated compounds (i.e., methanol) from such fuels will reduce the retardation factors for polynuclear aromatic hydrocarbons (PAHs), and cause these compounds to coelute at an earlier time in the contaminant sites. It is evident that higher volume fraction of cosolvent will be most efficient in facilitating the elution of hydrophobic organic compounds. The accidental release of oxygenated fuels into a river or other surface water bodies with contaminated sediment can result in the release of HOCs into the water. This was observed

during a study of the solubilization of PAHs from contaminated sediment due to a spill of oxygenated fuel into a simulated river (sediment/water) system (Chen and Delfino, 1996). The environmental consequence of the release of such contaminants and their transport further downstream was evaluated (Chapter 2). In this study, the cosolvent effect on the leaching and facilitated transport of PAHs from contaminated soil in the groundwater/soil system will be examined.

The objective of this study was to investigate the redistribution and facilitated transport of PAHs from contaminated soil caused by cosolvent effects due to oxygenated fuel spills. Specifically, the phase redistribution of PAHs from contaminated soil upon the addition of oxygenated fuels was studied in packed columns to simulate the subsurface environment. The results are expected to provide fundamental information in terms of fuel spill remediation and allow further assessment of the environmental and health effects of spills and leaks of oxygenated fuels in the subsurface environment.

Theory

The effect of oxygenated compounds on fate and transport of HOCs in the subsurface environment can be summarized as several mechanisms. Oxygenated compounds, as cosolvents, will reduce the surface tension between the solution phase and immiscible organic contaminants. This will reduce the capillary forces by which free-phase fuel are trapped in the porous media, and facilitates the mobilization of residual HOCs.

The presence of oxygenated compounds can also affect the properties of naturally-occurring organic components of the soil, such as swelling of organic matter. The potential effect of the swelling of organic matter is the enhanced release of HOCs residing in the matrix of organic matter. Due to the greater diffusive mass transfer, the mass-transfer limitation of sorption and dissolution are reduced (Brusseau et al., 1991). Thus, it enhances the release of sorbed HOCs.

Oxygenated organic liquids (cosolvents) reduce the polarity of the solution phase; therefore, increases the solubility of HOCs. The effect of cosolvents on the solution-phase activity of organic compounds depends on the nature of the solute and solvent-cosolvent system. A simple relationship describing the influence of cosolvent on the solubility of a solute in the mixed-solvent system is the log-linear cosolvency model (Yalkowsky et al., 1972; 1976; Yalkowsky and Rubino, 1985; Fu and Luthy, 1986b; Rao, et al., 1991; Kimble and Chin, 1994):

$$\log S_m = \log S_w + \beta \sigma f_c \quad (4-1)$$

where S is the solubility of the solute in water (w) and mixed-solvent (m), β is an empirical coefficient that accounts for water-cosolvent interactions, f_c is the volume fraction of organic cosolvent in the aqueous phase, and σ represents the cosolvency power of the cosolvent.

The cosolvency power (σ) can be viewed as the hypothetical partition coefficient for the HOCs between a cosolvent and water. The logarithm of the ratio of HOC solubilities in pure cosolvent and in pure water (S_w) is equal to the cosolvency power (σ):

$$\sigma = \log (S_c/S_w) \quad (4-2)$$

where S_c is the solubility of the solute in pure cosolvent (Rao et al., 1990).

Due to the infinite solubility and relatively high polarity, little sorption onto soil is expected for methanol and ethanol. Miscible organic liquids affect the fate and transport of organic contaminants in the subsurface by altering the sorption characteristics of hydrophobic compounds. The sorption of HOCs by soil and sediments is inversely proportional to their aqueous solubility (Karickhoff et al., 1979; Karickhoff, 1981; Chiou et al., 1979; 1983; Schwarzenbach and Westall, 1985; Rao, 1990).

The sorptive uptake of nonionic organic compounds from water is controlled by the organic matter fraction of soils and sediments. Natural organic matter in soil or sediment appears to function as a partition medium for the dissolution of nonionic organic compounds (Chiou et al., 1979; 1983). The uptake of nonionic organic compounds by soils can be described by a linear equation,

$$S = K_p C \quad (4-3)$$

where S is the solute concentration in soil, C is the equilibrium solute concentration in water, and K_p is the sorption coefficient.

The addition of a cosolvent will result in a decrease in retardation and sorption coefficient (K_p). Such phenomena have been demonstrated by many researchers (Fu and Luthy, 1986b; Nkedi-Kizza et al., 1985; 1987; 1989). For the sorption of HOCs from aqueous-organic binary solvent mixtures, the sorption coefficient is predicted to decrease exponentially as the fraction of organic solvent increases. A log-linear cosolvency model has been established to relate the equilibrium sorption coefficient (K_p) to the volume

fraction of cosolvent from binary mixed solvent (Rao et al., 1985; 1990; Kimble and Chin, 1994). The equation is expressed as:

$$\log K_{p,b} = \log K_{p,w} - \alpha\beta\sigma f_c \quad (4-4)$$

where $K_{p,b}$ and $K_{p,w}$ are the equilibrium sorption constants for the binary solvent and aqueous systems, respectively, α is a nonideality coefficient that accounts for cosolvent-sorbent interactions, β accounts for water-cosolvent interaction as defined in eq (4-1), and σ is the cosolvency power of the cosolvent.

The decrease in K_p caused by addition of a cosolvent results in a reduction in retardation. For transport problems, equilibrium sorption is commonly expressed in terms of a retardation factor (R) which represent the residence time of a chemical in pore volumes:

$$R = 1 + \rho K / \theta \quad (4-5)$$

where θ is the volumetric water content (mL/cm^3), and ρ the dry bulk density (g/cm^3).

Material and Methods

Contaminated Soil

Coal tar contaminated soil from Waterloo, Iowa was used to study the redistribution of polynuclear aromatic hydrocarbons (PAHs) in soil and aqueous phases in a packed soil column system. The physical and chemical properties of the contaminated sediment were determined prior to the initiation of experiments. Due to the extremely large retardation factors which result from the high coal tar content, it makes column experiments very impractical. Thus, in order to reduce the sorption capacity of the tar soil, contaminated

soil was prepared by mixing 20 grams of the coal tar contaminated soil with 180 g of a builder's sand (<1 mm) that was free of organic carbon. The sand was sieved (< 1 mm), prewashed by deionized water, and oven dried at 105 °C. The samples of contaminated soil (10% Waterloo soil and 90% clean sand by weight) were employed to simulate the contaminated subsurface environment by packed column experiment. Eighteen target polynuclear aromatic hydrocarbon (PAH) compounds were studied (Table 4-1). Based on the chemical characterization of the soil, the total PAH content (sum of eighteen PAHs) in contaminated soil was approximately 1200 mg/kg (Table 4-2). The relative distribution of PAHs by number of rings is shown in Figure 4-1.

Oxygenated Fuels

The oxygenated compounds used in the study were methanol, ethanol, and methyl tert-butyl ether (MTBE). Unleaded gasoline (93 octane) was obtained from a local service station. Gasoline composition was monitored prior to experiments to make sure none of the above additives were in the gasoline. Oxygenated fuels were prepared by mixing gasoline and oxygenated compounds in the laboratory. Oxygenated fuels selected in this study included two alternative fuels (M85 and E85) and oxygenated gasoline. The M85 and E85 were specifically selected as the alternative fuels to evaluate their performance under the original guidelines of the Alternative Motor Fuels Act of 1988 and the Energy Policy Act of 1992. The M85 and E85 fuels contain 15% gasoline, and 85% methanol or ethanol, respectively. The oxygenate, MTBE, was added to gasoline to a total of 15% by volume to form the oxygenated gasoline.

Table 4-1. Selected properties of PAH compounds investigated in this study.

Compound	MW (g/mole)	mp ^a (°C)	Solubility ^a (mg/L)	log K _{ow}
1. naphthalene	128.18	80.5	32	3.36
2. 2-methylnaphthalene	142.20	34.6	26	3.86
3. 1-methylnaphthalene	142.20	-22.0	27	3.87
4. acenaphthylene	152.20	92-93	3.93	4.07
5. acenaphthene	154.21	95	3.47	3.92
6. fluorene	166.22	116.5	1.9	4.18
7. phenanthrene	178.24	98-100	1.18	4.52
8. anthracene	178.24	216.3	0.073	4.54
9. fluoranthene	202.26	107	0.26	5.22
10. pyrene	202.26	149-151	0.16	5.18
11. benzo(a)anthracene	228.30	155-157	0.010	5.61
12. chrysene	228.30	254	0.006	5.61
13. benzo[b]fluoranthene	252.32	163-165	0.014	6.57
14. benzo[k]fluoranthene	252.32	217	0.00055	6.85
15. benzo[a]pyrene	252.32	179	0.003	6.04
16. indeno[1,2,3-cd]pyrene	276.34	160-163	0.062	7.70
17. dibenzo[a,h]anthracene	278.35	269-270	0.0005	6.36
18. benzo[ghi]perylene	276.34	278-280	0.00026	7.10

a From Data from Groundwater Chemicals Desk Reference, Montgomery and Welkom (1990).

Table 4-2. Chemical characterization of the contaminated soil used in this study.

Compound	Concentration* (mg/kg, dry weight basis)	Weight percentage (%)
1. naphthalene	202±6.76	18.2
2. 2-methylnaphthalene	111±3.46	10.1
3. 1-methylnaphthalene	76.7±2.60	6.92
4. acenaphthylene	19.1±1.18	1.72
5. acenaphthene	18.8±0.660	1.69
6. fluorene	67.1±2.60	6.05
7. phenanthrene	191±7.48	17.2
8. anthracene	29.7±1.23	2.68
9. fluoranthene	89.5±3.85	8.07
10. pyrene	115±3.53	10.4
11. benzo(a)anthracene	45.0±2.64	4.06
12. chrysene	44.3±2.20	3.99
13. benzo[b&k]fluoranthene	21.9±1.04	1.98
14. benzo[a]pyrene	42.7±1.69	3.85
15. indeno[1,2,3-cd]pyrene	4.73±1.12	0.43
16. dibenzo[a,h]anthracene	16.5±3.56	1.49
17. benzo[ghi]perylene	13.6±0.810	1.23

* Based on results of four replicates.

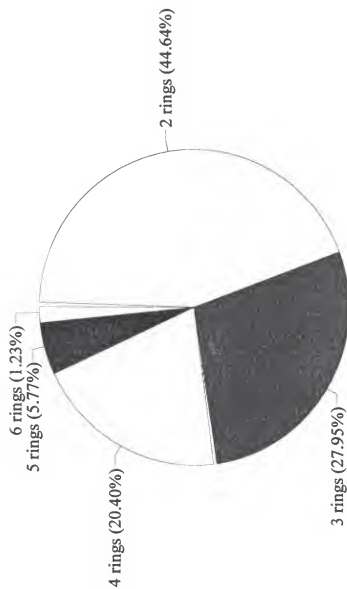


Figure 4-1. The relative distribution of PAHs by number of rings.

Column Experiments

Low Contaminated Soil Column

The miscible displacement technique (Lee et al., 1988; Brusseau et al., 1990) was used for all experiments. This technique involves the displacement of a solution through a column packed with the material of interest. A preliminary column experiment was conducted to illustrate the effects of single contaminant elution from soil by cosolvent flushing. A column was packed with clean sand and spiked with a known amount of naphthalene by pumping water with saturated naphthalene solution through the column. The sample of builder sand was packed in a glass column (diameter 2.5 cm, length 5.5 cm, Kontes Scientific Glassware, New Jersey). The column had Teflon® endplate fittings that were held in place by screw caps. The column was saturated overnight by flushing with an aqueous 0.01 N CaCl_2 solution. Once the soil was saturated, the column was placed in a horizontal position to minimize density-driven flow patterns. Pentafluorobenzoic acid (PFBA) was used as a non-reactive tracer to determine the hydrodynamic dispersion characteristics of the water-saturated column. The breakthrough curve for a pulse of PFBA was used to estimate the Peclet number (P) for the soil column ($P = 76$).

The water in the soil column was then displaced with an aqueous naphthalene solution ($C_o = 28$ to 30 mg/L) in a 0.01 N CaCl_2 aqueous matrix. The primary phase of the experiment was initiated by introducing mixed solvent (oxygenated compound plus water) at the column inlet. Mixed solvents selected in this experiment include 85% methanol, 85% ethanol, and saturated MTBE solution (5.8%). The cosolvent solution was applied for at least 3 hours (about 9 pore volumes) at a flow rate of 0.5 mL/min. The column effluent was

collected in a 2 mL vial using ISCO (Retriever 500) fraction collector every four minutes. The effluent samples were then analyzed by gas chromatography. After the experiment, the column was flushed with water over night, then saturated with aqueous naphthalene solution again for the next oxygenated compound.

Coal Tar Contaminated Soil Column

Potential spills of oxygenated fuels in a contaminated subsurface environment were simulated in the laboratory. Columns packed with contaminated soil (10% Waterloo soil and 90% clean sand by weight) were employed to simulate the contaminated subsurface environment. Each column was only used for one oxygenated fuel spill experiment. The dimensions of the glass column were described above. The columns were saturated with degassed 0.01 N CaCl_2 solution under continuous flow conditions (with flow rate of 0.5 mL/min) for three hours. It is assumed that the content of oxygenated compound would be constant all along the flow path to represent a large scale of fuel spill/leak. Continuous injection of oxygenated fuel was applied to represent an oxygenated fuel leak or spill to the subsurface environment. Oxygenated fuel was injected into the column in a flow rate of 0.5 mL/min for three hours (about 9 pore volumes). Mobilized PAHs were either re-sorbed onto the soil or will transport with the contaminant plume. The effluent from the soil columns was collected continuously every 4 minutes. The effluents were stored in 2 mL glass vials with Teflon® lined septa at 4 °C before PAH analysis.

After stopping injection of oxygenated fuels, water (containing 0.01 N CaCl_2) was pumped through the columns for three hours. This represents groundwater flow past the fuel spill (codisposal) site when leaking/spill fuel was stopped from spill site. The aqueous

samples were collected every 20 min, which required extraction prior to analysis due to high water content.

Two control experiments were conducted following the same protocol as described above for simulated spill experiments. For the first control set, the major difference is that instead of using oxygenated fuels, a mixed solvent (oxygenated compound plus water) was injected into the soil column. Also after certain pore volumes of injection (about 10 pore volumes), the injection was stopped and the column was closed on both ends. Then the following day, cosolvent was injected into the column again. By using a flow interruption technique, the sorption nonequilibrium in the soil column can be evaluated (Brusseau et al., 1989). This experimental design is similar to application of solvent flushing to contaminated soil. It served as a “contrast” set to evaluate the cosolvent effect under no influence of fuel constituents. The second control experiment was conducted using regular gasoline to simulate the spill of gasoline in contaminated subsurface environment. It served as a mass balance purpose to evaluate the transport of contaminants in the absence of cosolvent effect.

PAH Analysis

The aqueous samples from the MTBE flush experiment were extracted using 15 mL centrifuge tube with 2 mL of methylene chloride by rotary shaking. The extracts were transferred to 2 mL crimp-seal vials with Teflon® lined septa and refrigerated (4°C) until analysis.

Soils from the column experiments were extracted using a batch extraction method developed in earlier study (Chen, et al., 1996). Approximately 5 g of soils were placed in 35-mL Kimax tubes, and sequentially extracted with 1:1 v/v methanol-methylene chloride. The first extraction step involved equilibration with 25 mL of the solvent mixture for one day on a rotary shaker. Two sequential extractions involved 18-hr equilibrations with 10 mL of the solvent mixture. After each extraction step, the soil was centrifuged (626 g) for 30 min, and the supernatant was passed through a Teflon® filter (0.20 µm). Extracts were passed through a sodium sulfate column to remove residual water and then stored in bottles with Teflon® lined septa at 4°C. Extracts from each equilibration step were analyzed separately, i.e., extracts were not combined.

The effluent and soil extracts were analyzed by gas chromatograph/ flame ionization detector (GC/FID). The GC/FID analysis was performed using a Shimadzu GC-14A coupled to a Shimadzu AOC-14 autoinjector and CR601 data processor. The GC column was a 0.33 mm i.d., 30 meter, fused silica DB-5 (5% phenyl-95% methyl) column with a 1.0 µm film thickness purchased from J & W Scientific (California, USA). One microliter injections were made onto a GC column it had a 0.25 µm film thickness. The temperature gradient consisted of a 2 min hold time at 50°C, a ramp to 130°C at 30°C/min followed by 3 min hold time, a ramp to 240°C at 7°C/min, and a final ramp to 285°C at 12°C/min with an 8 min hold time. Both injector and detector temperatures were maintained at 260°C.

The PAH composition in gasoline was analyzed by GC/ITD. Gasoline diluted in methylene chloride (1:10 dilution) was injected into a Varian Saturn II GC/ITD with a

Varian Model 8100 autosampler. Analytical separation was achieved with a 0.25 mm i.d., 60 meter, fused silica DB-5MS (5% phenyl-95% methyl) column with a 0.25 μ m film thickness (J & W Scientific). The temperature program included a 5 min hold time at 50°C, temperature ramping at 30°C/min to 130°C followed by 3 min hold time, then temperature ramping at 5°C/min to 285°C, and a final temperature ramp at 1°C/min to 300°C with 20 min hold time. Helium was the carrier gas at a flow rate of approximately 1.0 mL/min. The electron energy was set at 70 eV. The electron multiplier voltage was 1650 V, and the transfer line temperature was 275°C.

Results and Discussion

Liquid samples from the column effluent, collected during both fuel spill or cosolvent flushing, and water flushing periods, were analyzed for the target eighteen PAH compounds listed in Table 4-1. The results can be used to evaluate the enhanced dissolution of PAHs and mass removal efficiency by the cosolvent flushing and the fuel spill in a contaminated subsurface environment.

The experimental data generated from the elution of naphthalene by three oxygenated compounds are shown in Figure 4-2. Release of naphthalene is relatively fast when flushing with 85% methanol, 85% ethanol, or 5.8% MTBE compared to normal aqueous dissolution rate. In the soil system with single contaminant, mobilization of naphthalene tends to be easier compared to the system with a more-hydrophobic organic compound. It was found that cosolvents had very little effect on the hydrodynamic parameters for the packed material (Wood et al., 1990). Therefore, through the experiments it was assumed

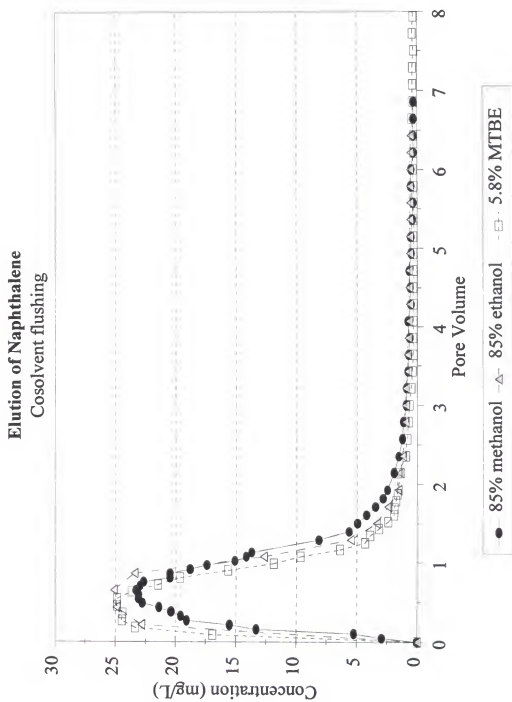


Figure 4-2. Elution profile of naphthalene by cosolvent flushing.

the Peclet number to be constant for various cosolvents by using the same soil column. The MTBE has the largest cosolvency power to PAHs among three oxygenated compounds ($\sigma_{\text{MeOH}} = 3.72$, $\sigma_{\text{EtOH}} = 3.99$, $\sigma_{\text{MTBE}} = 4.06$ for naphthalene), and ethanol has slightly higher cosolvency power compared to methanol due to its lower polarity (Chen and Delfino, 1996). Naphthalene eluted at earliest time by MTBE flushing in the elution profile. However, at high cosolvent content such as 85% methanol and ethanol used in this study, retardation factors for naphthalene are reduced to values close to 1, causing naphthalene to elute at an earlier time. Due to the low sorption onto builder sand, there is no significant difference in terms of elution profile of naphthalene by these three solvents.

Cosolvent Flushing

The dissolution of PAHs from coal tar contaminated soil by solvent flushing of oxygenated compounds is shown in Figure 4-3. The complete elution profiles of 18 PAHs are illustrated in Appendix C. When oxygenated compounds are introduced into the soil, the ganglia of coal tar (if free coal tar phase exists) will dissolve and decrease in size. The shrinking ganglia reduce the contact area between the solvent mixture and coal tar, which reduces the rate of dissolution.

With a non-uniform coal tar distribution, nonequilibrium dissolution may result due to both of large-scale effects (e.g., access to coal tar regions) and small-scale effects (e.g., diffusion within coal tar) in a heterogeneous domain. When significant nonequilibrium conditions for coal tar dissolution exist during flow, substantial concentration spikes in effluent are observed when flow is resumed following a quiescent period (Brusseau et al.,

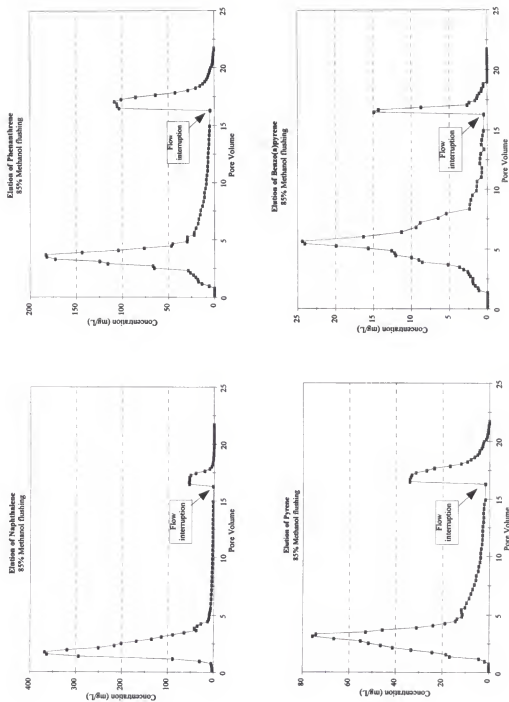


Figure 4-3. Elution profile of PAH compounds due to cosolvent flushing.

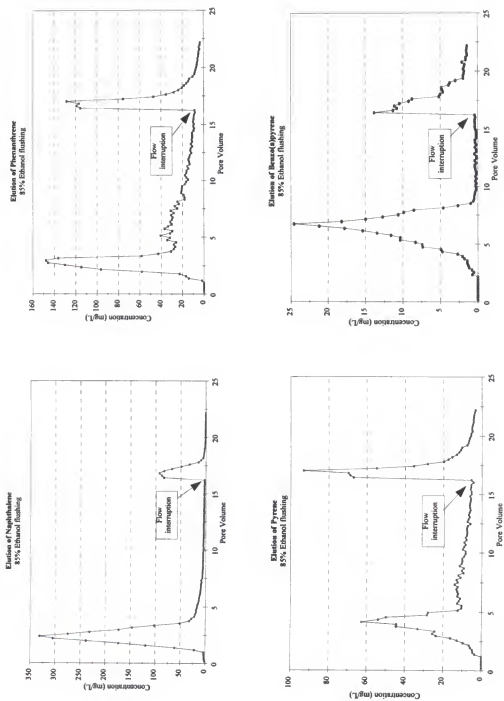


Figure 4-3. (Continued).

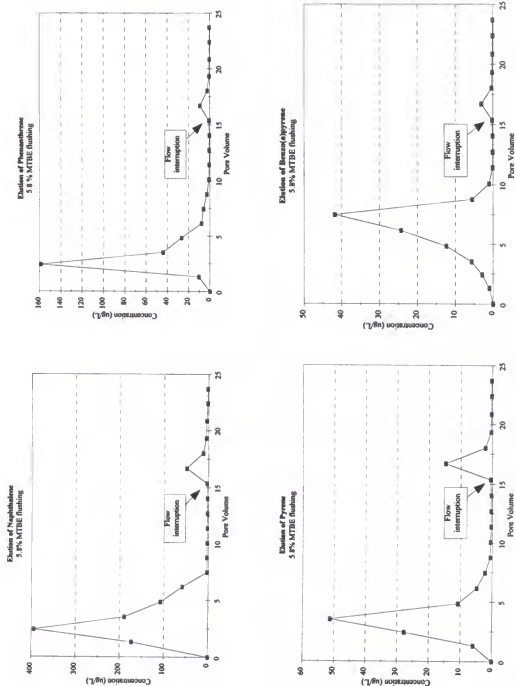


Figure 4-3. (Continued).

1989). This is the reason why applying flow interruption techniques, the apparent PAH concentration increase (concentration spike) was observed. Under the nonequilibrium condition, immobile zone was blocked by coal tar ganglia which cosolvent was not effective. On the other hand, a smaller volume of coal tar in a pore makes the pore more accessible for flowing water, which means an increasing contact area between the coal tar and mobile water. When the ganglia becomes smaller, the capillary pressure also decreases, which could mobilize the coal tar and transport it as a blob to another location in the porous medium where it gets trapped or joins another ganglia of coal tar. The increase in concentration of the coal tar constituents in the early part of the elution profile is due to increase in mole fraction of the large components as the more-soluble component are depleted. The magnitude of the concentration spikes may also related to the hydrophobicity of the coal tar constituents. Relatively greater response (Figure 4-3) was observed for the more-hydrophobic PAHs.

Addition of a cosolvent also reduces the surface tension between the coal tar and solvent mixture. This also leads to a reduction of the capillary pressure, and facilitates mobilization of the coal tar constituents. The cosolvent may partition into coal tar phase, lowering the mole fraction of other constituents. These phenomena described above make the dissolution process very complex but generally lead to an enhanced recovery of the coal tar.

Since the addition of a cosolvent increases the solubility of all constituents, it is expected that significant amounts of hydrophobic compounds will be removed from the coal tar phase. Moment analysis was employed to evaluate the mass removal efficiency in

cosolvent flushing experiment (Valocchi, 1985; Goltz and Roberts, 1987). The residual PAHs in the soil after cosolvent flushing was extracted and analyzed by GC/FID. The mass removal efficiency of PAHs by cosolvent flushing is shown in Table 4-3. Compared the removal efficiency of same compound by various cosolvent flushing, it is noted ethanol has largest removal efficiency. The MTBE has the highest cosolvency power among the three cosolvents, but the partially-miscible nature limits the volume fraction been able to apply in solvent flushing. Therefore, MTBE has the lowest mass removal efficiency. The removal efficiency decreases with the increase of molecular weight (i.e., more-hydrophobic PAH with higher K_{ow}). Because the solvent applied in this study is water-miscible, the concentration of less-hydrophobic PAHs partitioning into cosolvent phase will be larger than high K_{ow} compounds. Generally for compounds have relatively high solubility, the removal efficiency is very high. Given the condition using ethanol, the partitioning of more-hydrophobic compounds will show larger magnitude compared to methanol and MTBE flushing. By evaluating the moment analysis results, the mass removed by cosolvent flushing plus the mass remaining in soil (residual mass) should equal to original mass in soil (original PAHs in contaminated soil). However, mass unbalance was observed for few compounds. Possible factors for such effect may be contributed by analytical artifacts such as incomplete extraction recovery while analyzed residual PAH concentration in soil after flushing experiment. Also higher dissolution rate may occur for less hydrophobic compounds (e.g., naphthalene) when applying water to saturate the soil column prior the cosolvent flushing.

Table 4-3. The removal efficiency of PAHs from coal tar contaminated soil by cosolvent flushing.

	MeOH flushing				EtOH flushing				MTBE flushing			
	Mass in Soil	Moment analysis	Residual Mass	Removal Efficiency	Mass in Soil	Moment analysis	Residual Mass	Removal Efficiency	Mass in Soil	Moment analysis	Residual Mass	Removal Efficiency
NAPHTHALENE	8.99	7.02	1.63	78.1%	8.89	7.58	0.98	85.3%	9.49	0.92	8.44	9.6%
2-METHYLNAPHTHALENE	4.96	4.88	0.13	98.2%	4.90	3.88	0.82	79.1%	5.24	0.51	4.48	9.7%
1-METHYLNAPHTHALENE	3.42	2.96	0.33	86.5%	3.38	2.78	0.45	82.3%	3.61	0.33	3.08	9.2%
ACENAPHTHYLENE	0.85	0.40	0.41	47.2%	0.84	0.42	0.40	49.3%	0.90	0.04	0.82	4.6%
ACENAPHTHENE	0.84	0.74	0.07	88.0%	0.83	0.72	0.07	86.6%	0.88	0.07	0.70	8.4%
FLUORENE	2.99	2.09	0.51	69.9%	2.95	2.57	0.51	86.9%	3.15	0.30	2.52	9.6%
PHENANTHRENE	8.49	6.26	2.07	73.7%	8.39	6.22	1.77	74.1%	8.96	0.79	7.63	8.8%
ANTHRACENE	1.33	0.81	0.40	61.1%	1.31	0.97	0.42	73.9%	1.40	0.08	1.32	5.7%
FLUORANTHENE	3.99	2.36	1.45	59.2%	3.94	2.38	1.38	60.4%	4.21	0.33	3.62	8.0%
PYRENE	5.12	2.74	2.11	53.4%	5.06	3.19	1.35	62.9%	5.41	0.44	3.92	8.1%
BENZO(a)ANTHRACENE	2.00	0.89	0.75	44.5%	1.98	0.99	0.87	49.9%	2.11	0.14	1.71	6.3%
CHRYSENE	1.97	1.07	0.63	54.1%	1.95	1.09	0.74	56.1%	2.08	0.14	1.70	6.7%
BENZO(b&k)FLUORANTHENE	0.98	0.57	0.41	58.6%	0.97	0.51	0.46	53.2%	1.03	0.06	0.85	5.6%
BENZO(a)PYRENE	1.90	0.98	0.85	51.5%	1.88	1.06	0.64	56.1%	2.01	0.15	1.83	7.4%
INDENO(1,2,3-cd)PYRENE	0.21	0.05	0.11	22.3%	0.21	0.08	0.12	36.4%	0.22	0.01	0.16	6.3%
DIBENZO(a,h)ANTHRACENE	0.74	0.21	0.48	28.2%	0.73	0.24	0.38	33.1%	0.78	0.05	0.67	6.7%
BENZO(ghi)PERYLENE	0.61	0.12	0.47	20.2%	0.60	0.29	0.31	48.5%	0.64	0.04	0.62	5.9%

Four compounds (naphthalene, phenanthrene, pyrene, and benzo(a)pyrene) were selected to represent various degree of hydrophobicity of PAHs (log K_{ow} range from 3.36 to 6.04, ring number from 2 to 5) to examine the elution profiles by using the relative (normalized) concentration of each component versus pore volume (Figure 4-4). In the case of using cosolvent flushing, the elution of PAH components acts as “chromatographic effect”. The dissolution of PAH components will depend on the chemical properties such as hydrophobicity. It is noted that the solvents applied in this study may not be strong enough to make the partition of various PAH components into cosolvent reaching same order of magnitude. Thus, with various degree of partition of naphthalene, phenanthrene, pyrene, and benzo(a)pyrene into cosolvents (methanol, ethanol or MTBE), the elution profile shows the so called chromatographic effect. It is evident that the mobilization of PAHs depends on the solubility and total mass of coal tar. Overall, the less-hydrophobic compounds will be flushed out first, the opposite is true for more-hydrophobic compounds. Such effect will increase the difficulty in terms of remediation. Thus, in the field application of soil and groundwater remediation, methanol and ethanol may not be the proper cosolvents for the purpose of in-situ remediation.

Oxygenated Fuel Spills in the Subsurface Environment

The major source of oxygenated compounds are likely associated with the distribution, storage, and use of oxygenated fuels. Releases of oxygenated fuels to the subsurface from underground storage tanks, pipelines, and refueling facilities provide point source for entry of oxygenated compounds as well as gasoline hydrocarbons into

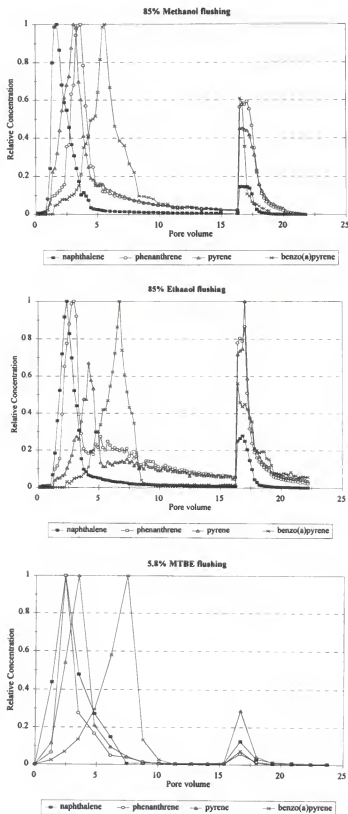


Figure 4-4. Normalized elution profile of PAH compounds by cosolvent flushing.

the hydrological cycle. In the case of an oxygenated fuel spill in the contaminated site, two counteracting processes will be involved: (1) hydrophobic fuel constituents (e.g., aromatic compounds) will contaminate the spill site, and (2) oxygenated compounds from fuel, acting as cosolvent, will facilitate the release of PAHs causing the increased effluent concentration of PAH compounds. When spilled oxygenated fuels encounter contaminated soil, or aquifer material, the aqueous concentrations of PAHs that previously sorbed onto soil increase in logarithmic fashion due to the solubility enhancement by completely or partially miscible oxygenated compounds from fuels following the manner of eq (4-1).

The facilitated transport of four representative PAH compounds from coal tar contaminated soil due to spill or co-disposal of oxygenated fuels and gasoline is shown in Figure 4-5. The complete elution profiles are illustrated in Appendix C. In a simulated fuel-spill experiment, the concentration of each constituent would increase sharply over the first few pore volumes as the fuel front progresses through the column. In terms of concentration level, the apparent difference was obvious between Figures 4-3 and 4-5 for compounds such as naphthalene and methyl substituted naphthalenes. For compounds such as naphthalene and methyl-substituted naphthalenes, the effluent concentration increases and reaches a plateau in the elution profile during the first few pore volumes. These fuel constituents will continuously contaminate the soil as long as the fuel spill is not terminated. Once the fuel spill stopped and with water flushing into the system, the elution of PAHs goes back to normal dissolution rate. It should be noted that the spill simulation conducted here only represent the scenario near the spill site. The effluent measured is composed of PAHs by two processes: (1) dissolution of coal tar constituents from

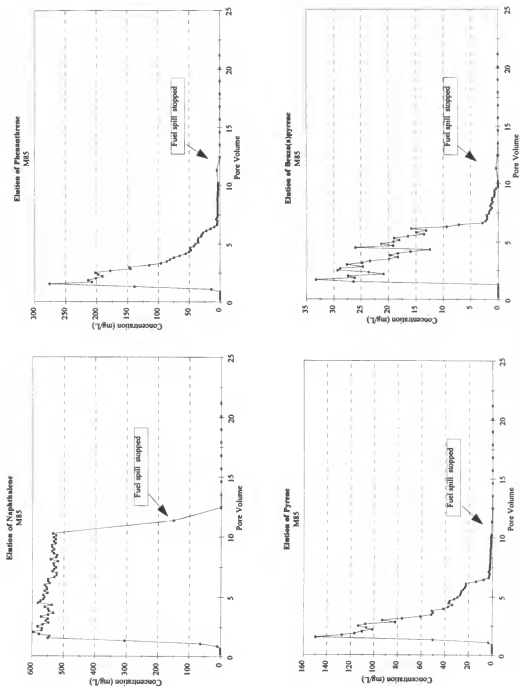


Figure 4-5. Elution of PAH compounds due to spill of oxygenated fuels and gasoline.

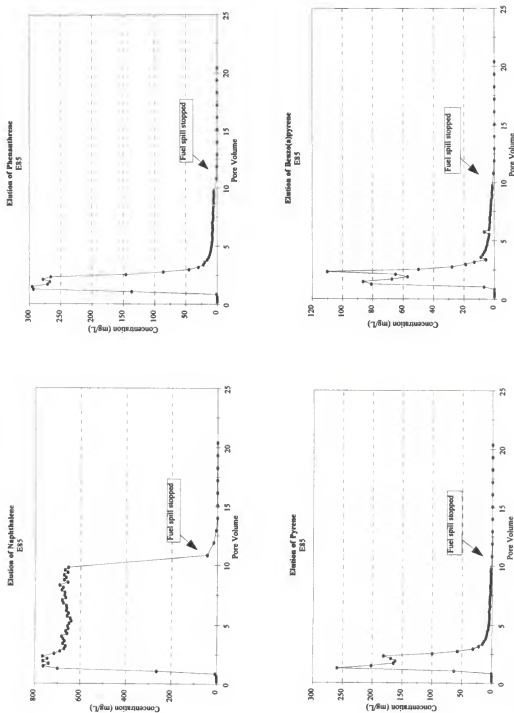


Figure 4-5. (Continued).

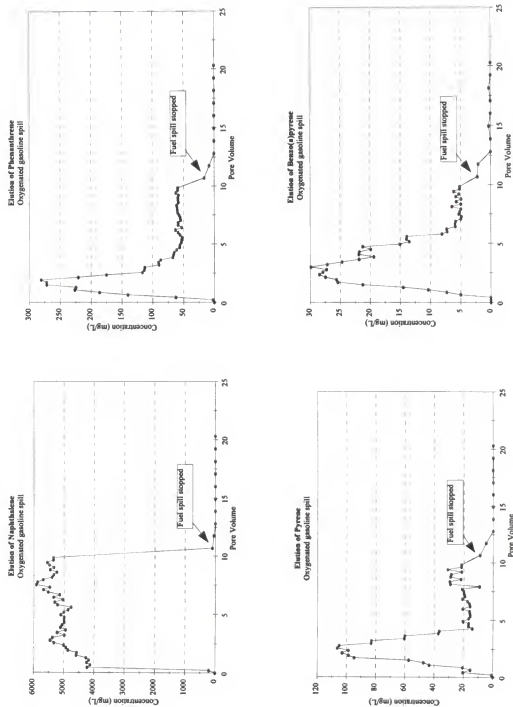


Figure 4-5. (Continued).

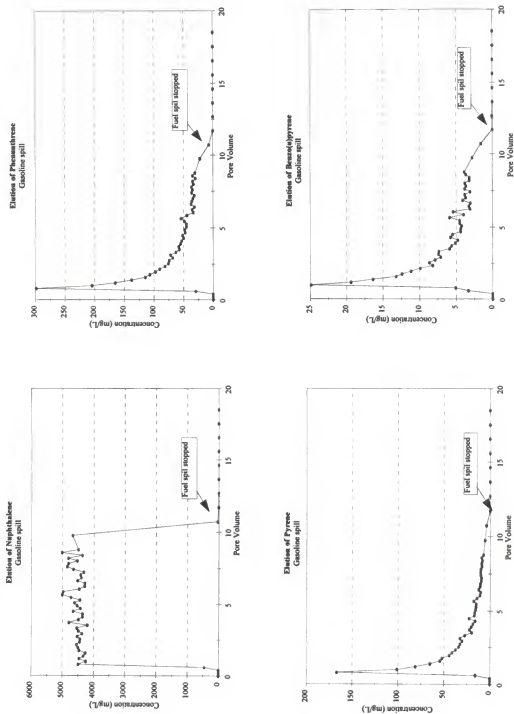


Figure 4-5. (Continued).

contaminated soil, and (2) transport of fuel constituents. Thus, the increased effluent concentrations of several PAHs (i.e., naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene) which are relatively more soluble and abundant among the fuel constituents will reach a plateau in elution profiles. For these components, the effluent concentrations measured will include the mobilized coal tar constituents which partition into oxygenated fuel phase and PAHs originated from fuel constituents. However, for the rest of PAHs which are not abundant in the fuel constituents, the elution profile demonstrates the similar trend as the elution profile from cosolvent flushing experiment. Also it is expected that the residual PAH concentrations in soil are higher after the fuel spill than after solvent flushing, which was demonstrated by analyzing PAHs in the soils after column experiments.

In order to assess the elution profile, the zero moment analysis was conducted to calculate the "net" PAH mass mobilized by oxygenated fuels due to the spill. Several parameters are necessary to allow such evaluation. First, the basic information of the PAH composition in gasoline as shown in Table 4-4 will allow the estimation of the amount of PAH from various oxygenated fuels input to the soil column (PAH_{ai}) by simulated spills. Second, the original mass of PAHs in contaminated soil (PAH_{ai}) were obtained by chemical characterization as described by Table 4-2. The third parameter is the zero moment analysis from elution profiles of PAHs as illustrated in Figure 4-5. By the moment analysis (using effluent concentration measurement of ten pore volumes for all the fuels), the amount of PAHs in effluent (PAH_{fe}) is obtained. With all three parameters, the net PAHs mobilized by fuel spills and mass removal efficiency can be estimated by the following equation:

Table 4-4. The PAH composition in gasoline.

Compound	Average Concentration* (mg/L)
1. naphthalene	3320
2. 1-methylnaphthalene	1709
3. 2-methylnaphthalene	850.6
4. acenaphthylene	4.990
5. acenaphthene	24.17
6. fluorene	9.83
7. phenanthrene	4.48
8. anthracene	1.50
9. fluoranthene	4.17
10. pyrene	2.86
11. benzo(a)anthracene	0.272
12. chrysene	2.97
13. benzo[b&k]fluoranthene	4.88
14. benzo[a]pyrene	3.49
15. indeno[1,2,3-cd]pyrene	0.510
16. dibenzo[a,h]anthracene	0.120
17. benzo[ghi]perylene	0.57

* Results based on six replicates.

$$\text{Removal efficiency} = (\text{PAH}_{\text{fi}} - \text{PAH}_{\text{of}}) / \text{PAH}_{\text{ci}} \quad (4-7)$$

One assumption should be made is that the sorption of PAHs from fuel constituents onto contaminated soil is minor, and can be neglected. This assumption should be reasonable due to the nature of aging coal tar soil which soil particles were covered by coal tar, thus, making the sorption kinetic rate relatively slow. The mass removal efficiency of PAHs due to the oxygenated fuel spills is shown in Table 4-5.

Comparing the results of mass removal efficiency by fuel spill and cosolvent flushing using the basis of same pore volume, it was found oxygenated fuels acting as cosolvents shows larger cosolvency power in terms of PAHs removal. The amount of PAHs from coal tar contaminated soil partitioning into the fuel phase is larger than by applying single cosolvent flushing (partitioning of PAHs into cosolvent). This tendency was seen mainly for more-hydrophobic compounds (compounds with larger K_{ow}). In the gasoline spill experiment, it was found release of PAHs from coal tar can also be facilitated by regular gasoline. Immiscible gasoline constituents act as a cosolvent to enhance dissolution of PAHs from contaminated soils. Under this circumstance, gasoline might be considered as a form of pseudosolvent to mobilize PAHs in an impacted site.

The normalized elution profiles of four representative PAH compounds by cosolvent flushing are shown in Figure 4-6. Gasoline constituents (15% by volume in M85 and E85; or 85% in oxygenated gasoline) from oxygenated fuels enhance the dissolution of PAHs by increasing the partitioning of coal tar constituents into the fuel phase. With dual cosolvent effects by oxygenated compounds and gasoline constituents, the dissolution of PAH compounds from coal tar will show similarity in terms of elution.

Table 4-5. Comparison of Removal efficiency of PAHs due to oxygenated fuel spills and cosolvent flushing.

	(In percentage)						
	M85	E85	Oxygenated gasoline	Gasoline	Methanol 85%	Ethanol 85%	MTBE 5.8%
NAPHTHALENE	98.45	99.01	99.93	70.62	67.89	69.88	9.51
2-METHYLNAPHTHALENE	96.39	95.76	93.03	66.28	85.65	86.88	8.91
1-METHYLNAPHTHALENE	91.04	91.46	92.12	48.58	72.53	63.90	8.18
ACENAPHTHYLENE	81.51	86.80	98.10	13.87	35.95	26.99	3.65
ACENAPHTHENE	60.65	71.44	80.94	19.69	47.95	51.79	6.70
FLUORENE	55.41	57.07	88.79	23.93	52.10	61.30	8.65
PHENANTHRENE	57.08	55.83	99.42	10.88	47.10	43.56	5.02
ANTHRACENE	84.63	93.08	97.53	11.75	40.68	39.56	4.13
FLUORANTHENE	50.36	55.66	79.92	28.09	42.40	28.73	4.00
PYRENE	56.23	60.98	69.19	49.65	36.70	29.93	4.05
BENZO(a)ANTHRACENE	55.82	67.45	87.70	48.49	25.05	9.65	4.52
CHRYSENE	53.10	56.17	63.76	43.13	33.01	12.78	3.54
BENZO(b&k)FLUORANTHENE	52.36	73.68	81.70	32.20	30.92	29.84	3.63
BENZO(a)PYRENE	48.92	70.79	70.58	30.55	42.34	27.33	5.57
INDENO(1,2,3-cd)PYRENE	63.24	71.89	81.26	11.85	15.17	18.23	2.83
DIBENZO(a,b)ANTHRACENE	54.04	47.68	46.62	8.66	19.28	10.58	3.99
BENZO(ghi)PERYLENE	59.36	57.91	50.49	7.75	13.16	40.97	5.15

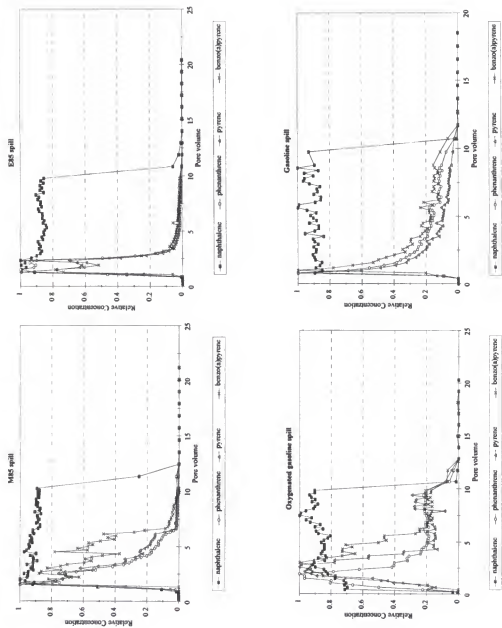


Figure 4-6. Normalized elution profile of PAH compounds due to spills of oxygenated fuels and gasoline..

Of the many compounds that make up coal tar, only a portion can be identified and quantified through chromatographic methods. When dealing with the complexity of oxygenated fuel spill in contaminated soil, it might be necessary to adopt the pseudocomponent concept to evaluate the dissolution of coal tar constituents under the influence of cosolvent. By examining the normalized elution profile, the breakthrough curves of compounds with close molecular weight (similar physical and chemical properties) can be treated as one curve. The effect and the extent to which multicomponent coal tar could be represented as a pseudocomponent in thermodynamic model was examined by previous investigators (Peters and Luthy, 1993, 1994). However, it might be reasonable to adopt pseudocomponent simplification for compounds which are not abundant in fuel constituents. In other word, it was found partition of more-hydrophobic PAHs into cosolvent phase are in the same order of magnitude.

The effect of fuel constituents and cosolvents on nonideality in the tar phase (represented by α) is unknown, and more research is necessary before this effect can be incorporated into the study as presented here. It is not obvious to draw conclusions for methanol or ethanol is better cosolvent in terms of facilitating transport of PAHs. However, MTBE has the highest cosolvency power. But the partial miscibility nature inhibits the removal efficiency. A mixture of oxygenated compounds will have higher cosolvency power to mobilize PAH, particularly large molecular weight PAHs. Such situations may exist in the case of spills of two fuel products.

Conclusion

The leak or spill of oxygenated fuel will produce the solvent flushing effect to the contaminated soil due to the high content of oxygenated compounds. The oxygenated compounds (methanol, ethanol, MTBE) from oxygenated fuels will reduce the retardation factors for PAHs, and cause these compounds to coelute at an earlier time. It is evident that higher volume fraction of cosolvent will be most efficient to facilitate elution of hydrophobic organic compounds.

With the potential problems as described above, clean-up operations involving oxygenated fuel spills may deal with more contaminants and higher aqueous concentrations than expected. Therefore, leaks and spills of an oxygenated fuel may increase the difficulty for clean-up and remediation. The study will assist the prediction of the fate parameters (i.e., dissolution, sorption) that might be used in regulatory decisions and health concern when oxygenated fuels are widely used.

CHAPTER 5

FIELD SCALE SPILL SCENARIOS

It is evident from the results in the previous chapters that oxygenated compounds from fuel spills will induce the facilitated transport of hydrophobic organic contaminants from impacted sites. Given the brief description of spill scenarios in Chapter 1, and the sequential laboratory experiments to evaluate the cosolvent effect when oxygenated fuel spills occur, the establishment of hypothetical spill scenarios is essential to quantitate field conditions. Thus, several case studies are used to represent oxygenated fuel spills in surface water systems and the subsurface environment.

Case I: Small Scale Spill of Oxygenated Fuel in a River System

This case represents the small scale spill of oxygenated fuels from a fuel truck into in a river. It is assumed that the bottom sediment of the river was contaminated as a result of earlier industrial operations. Thus, when 1000 L of M85 fuel spill into the river, the likely scenario will be similar to that addressed in Chapter 1. The alternative fuel (M85) was selected to be the representative oxygenated fuel in these scenarios. When gasoline constituents encounter water, the hydrophobic compounds will spread and form a thin film on top of the surface water due to the immiscibility between the hydrophobic components and difference of surface tension. The thin film will move downstream by hydrodynamic forces. A plume of water contaminated with oxygenated compounds will be characterized

by completely dissolved contaminants and will exhibit a density less than the density of uncontaminated water. After the oxygenated compounds completely dissolved in water (the equilibration rate is relatively fast), the contaminant plume will have a density between that of the pure oxygenated compound and that of river water. The contaminant liquid will mix through the water column and finally reach the bottom sediment. As the low-density miscible plume migrates a great distance from the spill area, the effect of hydrodynamic dispersion will be to dilute the plume, resulting in a lower volume fraction of cosolvent and the density returns close to that of water.

To assess the cosolvent effect of oxygenated compound when it contacts the contaminated sediment, the following equation (eq 5-1) is used to calculate the volume fraction of cosolvent (oxygenated compound) when the oxygenated compound is transported with water. As the oxygenated mass is transported through the flow system, the concentration distribution of the oxygenated compound at time t is given by (Fischer et al., 1979)

$$C(x, y, z, t) = \frac{m}{8} \left\{ \operatorname{erf} \left[\frac{(L + x) - vt}{2(D_x t)^{1/2}} \right] + \operatorname{erf} \left[\frac{(L - x) + vt}{2(D_x t)^{1/2}} \right] \right\} \\ \times \left\{ \operatorname{erf} \left[\frac{(M - y)}{2(D_y t)^{1/2}} \right] + \operatorname{erf} \left[\frac{(M + y)}{2(D_y t)^{1/2}} \right] \right\} \\ \times \left\{ \operatorname{erf} \left[\frac{(N - z)}{2(D_z t)^{1/2}} \right] + \operatorname{erf} \left[\frac{(N + z)}{2(D_z t)^{1/2}} \right] \right\} \quad (5-1)$$

where m is the mass of oxygenated compound introduced at the point source, D_x , D_y , and D_z are the dispersion coefficients in the x , y , z directions, v is the velocity, and x , y , and z are distances in three dimensions from the center of the gravity of the oxygenated compound mass. It is assumed that the initial distribution of an oxygenated compound as a rectangular prism source with length, width, and depth as $2L$, $2M$, and $2N$, respectively. It is apparent from eq 5-1 that the maximum concentration of oxygenated compound is located at the center of the contaminant plume. With this simplified hydrological setting, the preliminary estimates of the migration pattern of oxygenated fuel spill can be obtained to assist the quantitative aspect of fuel spill scenarios.

In this case study, the dimensions of the river are assumed to be 40 m in width with 10 m depth. The velocity of the river is 0.5 m/sec with $D_x = 0.4 \text{ m}^2/\text{sec}$, and D_y and D_z equal to $0.04 \text{ m}^2/\text{sec}$, respectively. The river was considered to be uniform and straight channel of constant depth. Under these conditions, the contour of cosolvent concentration is calculated by eq (5-1) and converted to volume fraction of cosolvent. When 1000 L of M85 fuel spill into the river from a fuel truck, the plume of cosolvent will travel relatively fast. As shown in Figure 5-1, the volume fraction of the methanol plume at 100 m away from spill site at a depth of 10 m is $5 \times 10^{-3} \%$. After ten minutes, it will travel 300 m downstream and will spread to an area of 70 m in length and 20 m in width. The volume fraction of methanol plume at 300 m away from the spill site at a depth of 10 m is $3 \times 10^{-3} \%$. It should be noted that the boundary effect (i.e., spreading of oxygenated is restricted by the presence of boundaries) of the river is neglected. If this effect (mirror image source effect) is

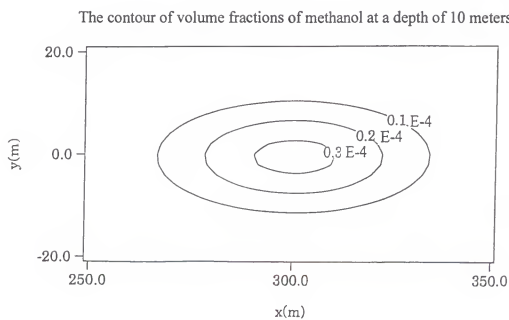
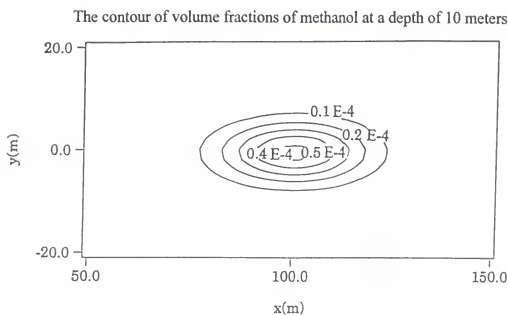


Figure 5-1. The contour of volume fraction of methanol at various distances from the spill site following 1,000 L of M85 spilled into a river.

considered, the volume fraction of oxygenated compound will be approximately four fold larger than the results which were simulated in the above case. The boundary effect will be accounted in all cases of fuel spill into river systems studied here. Thus, the volume fraction of methanol at a depth of 10 m is 2×10^{-2} % and 1.2×10^{-2} %, at 100 m and 300 m away from spill source, respectively. Given this minor fraction of cosolvent, the facilitated transport of hydrophobic organic compounds from bottom sediment is not meaningful.

Case II: Medium Scale Spill of Oxygenated Fuel in a River System

This case represents the medium scale spill of oxygenated fuels from a barge into in a river. The conditions of the river are the same as described in Case I. There are 100,000 L of M85 fuel spilled into the river from a barge. The initial distribution of an oxygenated compound is a rectangular prism source with length, width, and depth as 5m, 5m, and 4m, respectively. The volume fraction of the oxygenated compound plume at 100 m away from spill site at a depth of 10 m is 20 % (Figure 5-2). Since the volume fraction of methanol decreases with distances, it becomes 8 % at 300 m away from the spill site.

Assuming a highly hydrophobic organic contaminant with σ_{MeOH} equal to 7.0 in the contaminated sediment, the cosolvent effect will induce the solubility of this compound to increase 25 folds in river water at downstream 100 m, and 4 times of solubility enhancement at 300 m away from the spill site. For a less-hydrophobic contaminant with σ_{MeOH} equal to 3.5, the solubility will increase 5 and 2 folds at 100 m and 300 m away from the spill site, respectively. With the spill of 100,000 L of M85 into a river, likely the solubility enhancement of hydrophobic organic compounds from bottom sediment by

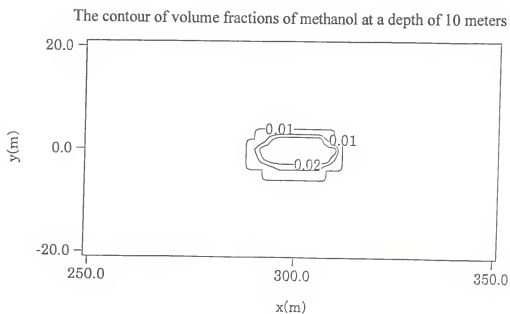
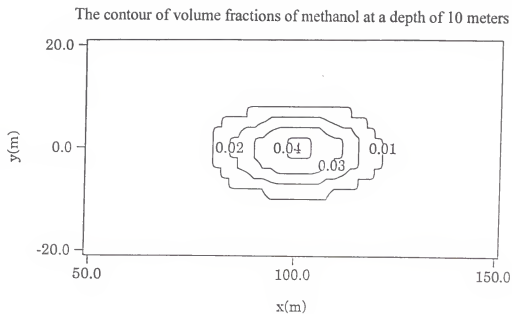


Figure 5-2. The contour of volume fraction of methanol at various distances from the spill site following 100,000 L of M85 spilled into a river.

oxygenated compound will be observed at a limited region downstream where it is close to the spill site. From the regulatory aspect, such facilitated transport of secondary contamination is important in terms of drinking water supply.

Case III: Large Scale Spill of Oxygenated Fuel in a River System

This case represents the catastrophic spill of oxygenated fuels from aboveground storage tanks into a river. A similar case was seen when an above ground storage tank collapsed in Floreffe, Pennsylvania in 1988. There were about one million gallons of diesel fuel spilled into the Monongahela River. The parameters of the river used in this case are the same as described in Cases I and II. Assume 1,000,000 L of M85 fuel spill into a river due to collapse of an aboveground storage tank. With the large amount of spill, it is assumed the initial distribution of an oxygenated compound is a rectangular prism source with length, width, and depth as 10m, 10m, and 10m, respectively. Thus, methanol will reach the bottom sediment right after the spill. Given the condition described above, the volume fraction of methanol in terms of travel distance is calculated by eq 5-1 and illustrated in Figure 5-3. As shown in Figure 5-3, the volume fraction of the methanol plume at 200 m downstream from the spill site at the depth of 10 m is 42 %. It was decreased to 20 % at 1000 m downstream from the spill site, and further to 10 % at 3900 m downstream from the spill site. Adopting the same contaminant parameters used in Case II, the solubility enhancement for a highly hydrophobic organic contaminant ranges from 5 to 871 times at this region. For the less-hydrophobic HOC, the solubility enhancement is 2 to 30 times at this region. Considering the impacted zone by methanol (about 4 km in length),

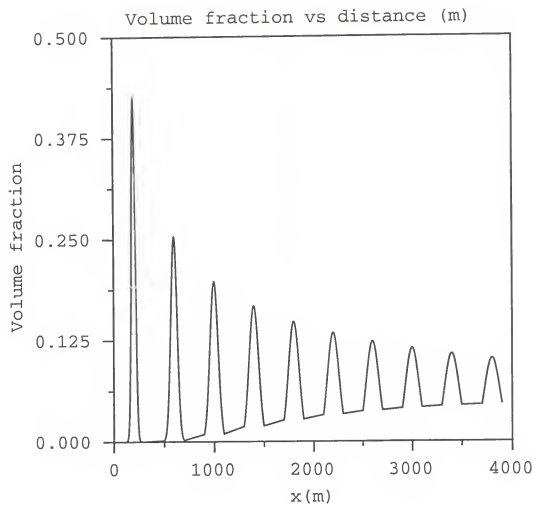


Figure 5-3. Volume fractions of methanol at various distances from the spill site following 1,000,000 L of M85 spilled into a river.

the facilitated transport of HOCs from contaminated sediment will be observed further downstream and eventually these contaminants will re-settle onto sediment once the cosolvent effect becomes negligible. Given this “spreading effect” induced by cosolvent, the magnitude of secondary contamination is relatively large compared to the above cases.

Case IV: Small Scale of Oxygenated Fuel Spill in the Subsurface Environment

This case represents the small scale spill of oxygenated fuels from an underground storage tank to subsurface environment. This scenario likely will be seen in service station locations when oxygenated fuels are distributed.

In the subsurface environment, groundwater contaminated with oxygenated compounds will be characterized by completely dissolved cosolvent (except MTBE) and will exhibit a density less than the density of uncontaminated water. Due to the properties of low density and infinite or high solubility, oxygenated compounds display a range of behavior when encountering groundwater. It should be noted that one characteristic behavior is the spreading of the oxygenated compounds by dispersive processes. After the oxygenated compounds completely dissolve in groundwater, the contaminant plume will have a density between that of the pure oxygenated compound and that of groundwater. After a low-density miscible plume has migrated a great distance from the source area, the effect of hydrodynamic dispersion will have diluted the plume, resulting in a density near that of fresh water. Also, the process of transverse dispersion will have contributed to the vertical spreading of the plume. At great distances from the source area, the plume will extend from the top of the aquifer to a depth greater than which was observed near the

source. Depending on the migration distance and the thickness of the aquifer, contamination may extend over the entire vertical thickness of the aquifer. The immiscible plume (fuel-related hydrocarbons) will tend to float on water due to its low density. The floating plume will be found at or near the water table and may locally disperse along the water table. The movement is controlled by gravity and the advective groundwater velocity.

To assess the cosolvent effect of oxygenated compounds in the subsurface environment when they contact the contaminated aquifer, the following equation (eq 5-2) is needed to calculate the volume fraction of cosolvent (oxygenated compound) when the oxygenated compound advects with water. As the mass of oxygenated compound is transported through the aquifer, the concentration distribution of the oxygenated compound at time t is given by (Freeze and Cherry, 1979)

$$C(X, Y, Z, t) = \frac{M}{n8(\pi t)^{3/2} \sqrt{D_x D_y D_z}} \exp\left(-\frac{X^2}{4D_x t} - \frac{Y^2}{4D_y t} - \frac{Z^2}{4D_z t}\right) \quad (5-2)$$

where M is the mass of oxygenated compound introduced at the point source, n is the porosity, D_x , D_y , and D_z are the dispersion coefficients in the x , y , z directions and X , Y , and Z are distances in the x , y , and z directions from the center of the gravity of the oxygenated compound. It is clear from eq 5-2 that the maximum concentration of oxygenated compound is located at the center of the contaminant plume.

In this case, it is assumed 1000 L of M85 fuel spill from an underground storage tank into the subsurface environment. The depth of the unconfined aquifer is 10 m with porosity equal to 0.3. The groundwater velocity is 0.1 m/day with $D_x = 0.005 \text{ m}^2/\text{day}$, D_y

and D_z equal to $0.001 \text{ m}^2/\text{day}$, respectively. The aquifer was previously contaminated by the disposal of hydrophobic organic contaminants. When 1000 L of M85 fuel spills into the subsurface environment from underground storage tank, the plume containing the oxygenated compound will travel with the groundwater. By the end of 50 days, the plume will travel about 5 m down gradient. Given the condition above, the contour of cosolvent concentration is calculated by eq 5-2.

As illustrated in Figure 5-4, the center concentration of methanol plume at 5 m from the spill site at a depth of 1 m is 46.72 kg/m^3 , which is equivalent to a volume fraction of 5.9 %. The actual volume fraction of cosolvent will be lower due to the spreading of the methanol plume. With the slow dispersion rate in the subsurface environment, the volume fraction of cosolvent becomes very small at a depth of 2 m (0.3 %) and 3 m (2.5×10^{-3} %), and is negligible below that. After a long period of time (300 days), the concentration of the oxygenated compound plume at 30 m from the spill site at a depth of 1 m is 7.3 kg/m^3 , which is equivalent to a volume fraction of 1.0 %. Thus, The volume fraction of cosolvent becomes insignificant at depths lower than that. the cosolvent effect in the case of small spill will only be seen at depth of 1 m, if the area of the down gradient aquifer was previously contaminated (residual contaminants).

If the unsaturated zone of the spill site was previously contaminated by diesel fuel, once the M85 spill occurred, the residual contaminants in unsaturated zone will transport (desorption rate increases) due to the cosolvent effect by methanol. These contaminants will infiltrate or percolate along with the spilled source to water table. Such scenario was demonstrated by column experiments in Chapter 4. Under this circumstance, the zone

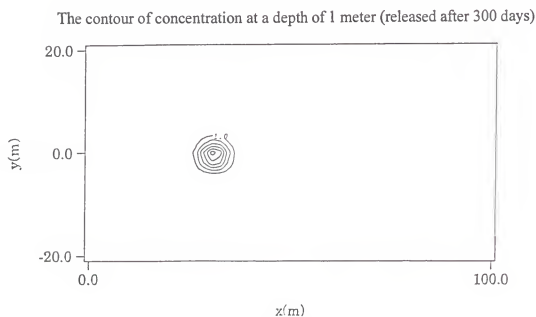
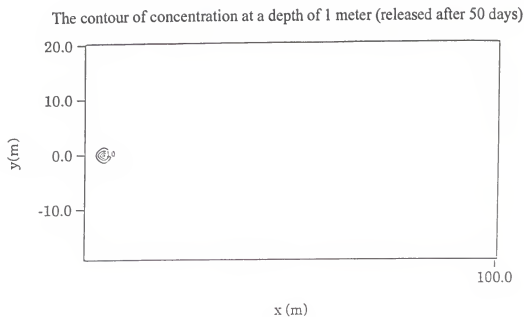


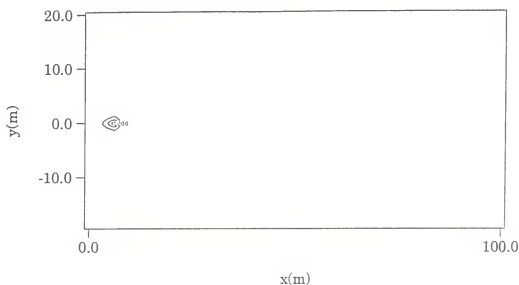
Figure 5-4. The contour of concentration of methanol following 1,000 L of M85 spill in the subsurface environment.

affected by oxygenated compound will be larger and not limited to the vicinity area of the groundwater table.

Case V: Large Scale Spill of Oxygenated Fuel in the Subsurface Environment

This case represents the large scale spill of oxygenated fuel in the subsurface environment resulting from a pipeline rupture. In this case, it is assumed 100,000 L of M85 fuel spill from a pipeline into the subsurface environment. The conditions of the unconfined aquifer and the groundwater parameters are similar as described in Case IV. When 100,000 L of M85 fuel spills into the subsurface environment, the plume will travel 5 m down gradient by the end of 50 days. The concentration of the oxygenated compound plume at 5 m from the spill site at a depth of 1 m is relatively high (volume fraction of cosolvent is about 50 %) (Figure 5-5). Because the plume did not spread out to a large area, the area influenced by the oxygenated compound is limited despite the large volume fraction of cosolvent. After a long period of time (300 days), the concentration of the oxygenated compound plume at 30 m from the spill site at a depth of 1 m is 100 kg/m³, which is equivalent to a volume fraction of 13 % and the volume fraction of cosolvent decreases with depth to an insignificant level at a depth lower than 5 m. Thus, in the case of a large spill, the cosolvent effect will be seen at the depths of 1 to 5 m, if the down gradient aquifer was previously contaminated. Due to the large amount of spill, the solvent flushing effect will be observed if the unsaturated zone was previously contaminated due to co-disposal operation. Thus, facilitated transport of HOCs will be observed at downgradient.

The contour of concentration at a depth of 1 meter (released after 50 days)



The contour of concentration at a depth of 1 meter (released after 300 days)

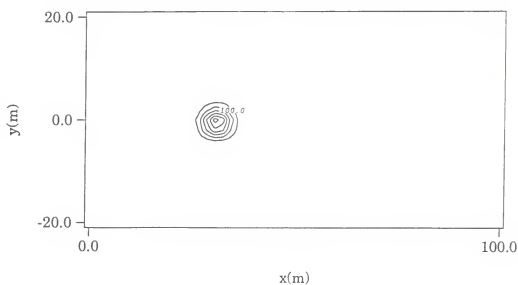


Figure 5-5. The contour of concentration of methanol following 100,000 L of M85 spill in the subsurface environment.

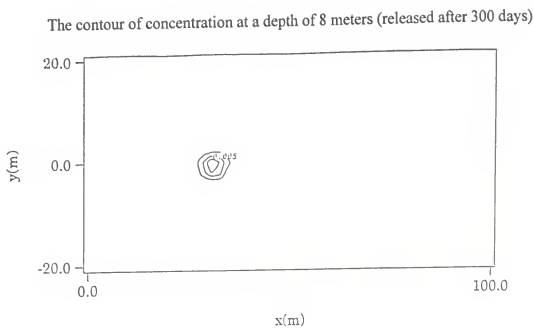


Figure 5-5. (continued).

The simulated cases in the subsurface addressed here are based on ideal conditions, such as the instantaneous released source and uniform flow. Such a quantitative assessment can be useful to obtain general estimates of the migration patterns of oxygenated compounds which may arise from oxygenated fuel spills in the surface and subsurface environments.

CHAPTER 6

SUMMARY AND CONCLUSIONS

Oxygenated Fuel Spills in River Systems

Cosolvents have been recognized to have a significant impact on the redistribution and movement of hydrophobic organic compounds (HOCs) in the environment. The cosolvent effect of oxygenated compounds (methanol, ethanol, and methyl tert-butyl ether (MTBE)) on the solubility of polynuclear aromatic hydrocarbons (PAHs) was examined by laboratory experiments. Coal tar contaminated sediment was used to study the redistribution and facilitated solubilization of 18 PAH compounds in both sediment and aqueous phases caused by cosolvent effects when oxygenated fuel spills occur.

The cosolvent effect can occur at various volume fractions of cosolvent, and not just occur at high volume fraction. However, at a low volume fraction of cosolvent, solubility enhancement will be difficult to determine for hydrophobic organic compounds (e.g., PAHs or PCBs) due to analytical constraints. Therefore, in the experimental design, the "worst case scenario" was simulated. The batch dilution experiment in this study was designed to represent a major spill in a river. Thus, a high fuel/water ratio (1:1 in volume) was selected to represent the spill site. The dilution effect for a real spill depends on the amount of fuel and the flow rate of a river. Thus, the cosolvent effect may vary depending on hydrodynamic parameters. To enable the cosolvent effect to occur, certain volume percentages of cosolvent are required in the system. Therefore, the

experiments represented a wide spectrum of volume fractions of cosolvent under various dilutions (e.g., 0.459, 0.184, and 0.0735 for methanol and ethanol).

The results indicate that PAH solubility increased essentially in a log-linear manner with an increased volume fraction of methanol and ethanol. Deviations from a log-linear relationship were observed for MTBE due to its limited aqueous solubility, and the cosolvent effect was seen only at the simulated fuel spill site. A linear relationship between the cosolvency power and the logarithm of octanol/water partition coefficient was observed.

Facilitated Transport of Hydrophobic Organic Compounds by Colloids

The significance of the colloidal phase in the redistribution of polynuclear aromatic hydrocarbons (PAHs) in a coal tar contaminated sediment/water system by introduction of oxygenated and alternative fuels was studied. The quantitation of colloids from a simulated river system was conducted through a batch dilution experiment in the laboratory. Ultrafiltration was employed to differentiate an aqueous phase sample into two subsamples (with and without colloids). A three-phase distribution (sediment-colloidal-aqueous phase) was applied to study the redistribution of PAHs from coal tar contaminated sediment by the introduction of oxygenated fuels.

This study demonstrated the results of combining the cosolvent effect and with the contribution of the colloidal phase in the mobilization and redistribution of PAHs from contaminated sediment. The cosolvent effect due to the oxygenated compounds facilitated the release of PAHs from coal tar contaminated sediment in a simulated fuel

spill. Solubility enhancement of PAHs was followed by the condensation of PAHs onto colloids in a simulated fuel spill. The results showed that the cosolvent effect dominates the role of colloids in the redistribution of PAHs. The cosolvent effect reduces the sorption of PAHs onto colloids. This effect constrained the significance of colloids in the transport of PAHs in the aqueous system.

Oxygenated Fuel Spills in the Subsurface Environment

The redistribution and facilitated transport of PAHs from contaminated soil caused by cosolvent effects related to oxygenated fuel spills was evaluated by miscible displacement techniques. Oxygenated fuel was continuously injected into a soil column to represent a fuel leak or spill to the subsurface environment. The leak or spill of oxygenated fuel induced the solvent flushing effect to the contaminated soil due to the high content of oxygenated compounds. The elution profile of 18 PAHs suggested that oxygenated compounds from fuel can serve as cosolvents that will enhance the dissolution of PAHs from contaminated soil when the fuel comes in contact with the contaminated soil. Mobilized PAHs are either re-sorbed later onto the soil down gradient or move with the groundwater flow. The oxygenated compounds from these fuels reduced the retardation factors for PAHs, and caused them to coelute at an earlier time. It was noted that immiscible gasoline constituents acted as a pseudosolvent to mobilize PAHs.

The alternative fuels (M-85 and E-85) used in this study are not now commercially available. However, these fuels might be used in the near future depending on a change in U.S. energy policy. The use of oxygenated fuels has received much attention in recent

years as a way to minimize combustion-related air pollution. The environmental impact of a probable fuel spill can be estimated from knowledge of environmental organic chemistry and the reactivity of fuel constituents in the aquatic system. The scenarios addressed here emphasized the significance of “secondary contamination” in aquatic and subsurface environment due to high oxygenate content in fuel when an oxygenated fuel spill occurs.

With the potential problems as described above, clean-up operations involving oxygenated fuel spills may deal with more contaminants and higher aqueous concentrations than expected. Therefore, the leak and/or spill of an oxygenated fuel may increase the difficulty for clean-up and remediation. This study provides fuel spill scenarios that can help to predict the facilitated transport of PAHs from coal tar contaminated sediment due to the cosolvent effects.

Conclusions

- In batch experiments, PAH solubility increased essentially in a log-linear manner with an increased volume fraction of methanol and ethanol.
- Deviations from a log-linear relationship in batch experiments were observed for MTBE due to its limited aqueous solubility, and the cosolvent effect was seen only at the simulated fuel spill site (high cosolvent volume fraction).
- A linear relationship between the cosolvency power and logarithm of octanol/water partition coefficient was observed.

- The cosolvent effect dominates the role of colloids (condensation of PAHs) in the redistribution of PAHs.
- The cosolvent effect reduces the sorption of PAHs onto colloids and constrains the significance of colloids in the transport of PAHs in the aqueous system.
- The leak or spill of oxygenated fuels induces the solvent flushing effect to the contaminated soil due to the high content of oxygenated compounds in the subsurface environment.
- The elution profile of 18 PAHs suggested that oxygenated compounds from fuel can serve as cosolvents that will enhance the dissolution of PAHs from contaminated soil when the fuel comes in contact with the contaminated soil.
- The oxygenated compounds from these fuels can reduce the retardation factors for PAHs, and cause these compounds to coelute at an earlier time.
- Immiscible gasoline constituents act as a pseudosolvent to mobilize PAHs and enhance desorption of PAHs.

APPENDIX

Table A-1. Sediment phase concentration in sediment/water partition experiment.

SAMPLE	(All unit in mg/kg)					
	P-1	P-2	P-3	P-4	P-5	P-6
NAPHTHALENE	89.3	99.8	99.8	100.2	105.9	98.9
2-METHYLNAPHTHALENE	78.1	82.1	83.8	95.3	94.9	91.0
1-METHYLNAPHTHALENE	77.5	76.0	82.6	82.2	78.4	76.2
ACENAPHTHYLENE	21.5	16.3	23.7	20.2	21.2	22.4
ACENAPHTHENE	31.6	39.2	40.3	39.2	39.6	31.2
FLUORENE	35.5	41.9	31.4	32.4	33.9	35.1
PHENANTHRENE	80.8	76.3	84.0	88.0	87.9	84.8
ANTHRACENE	29.4	21.3	26.2	30.2	25.5	22.4
FLUORANTHENE	58.1	54.1	62.9	52.5	56.0	51.4
PYRENE	85.7	95.0	85.6	93.1	94.2	97.1
BENZO(a)ANTHRACENE	37.8	33.1	37.2	40.3	44.7	36.8
CHRYSENE	31.3	30.9	39.7	33.5	40.4	31.1
BENZO(b)FLUORANTHENE	22.8	22.2	28.0	21.5	23.0	17.8
BENZO(k)FLUORANTHENE	14.9	19.2	15.1	14.5	15.1	15.9
BENZO(a)PYRENE	22.2	26.2	27.1	26.8	22.5	24.5
INDENOC(1,2,3-cd)PYRENE	12.7	13.8	15.0	15.1	18.6	16.3
DIBENZO(a,h)ANTHRACENE	7.37	8.38	7.56	10.1	7.79	8.25
BENZO(ghi)PERYLENE	17.8	20.1	14.4	16.9	18.3	16.9
Total PAH	754	776	805	812	828	778

Table A-2. Aqueous phase concentration in sediment/water partition experiment.

Sample	(All unit in mg/L)					
	PA-1	PA-2	PA-3	PA-4	PA-5	PA-6
NAPHTHALENE	6.67E-02	7.24E-02	7.21E-02	5.10E-02	8.91E-02	8.47E-02
2-METHYLNAPHTHALENE	5.33E-03	4.99E-03	5.10E-03	5.17E-03	7.20E-03	5.00E-03
1-METHYLNAPHTHALENE	4.61E-03	5.13E-03	4.45E-03	4.34E-03	6.00E-03	4.40E-03
ACENAPHTHYLENE	1.03E-03	1.03E-03	9.21E-04	1.00E-03	1.14E-03	1.00E-03
ACENAPHTHENE	9.99E-03	9.15E-03	9.02E-03	1.10E-02	1.27E-02	1.04E-02
FLUORENE	5.25E-03	5.32E-03	3.81E-03	6.37E-03	6.03E-03	4.61E-03
PHENANTHRENE	5.45E-03	7.17E-03	6.11E-03	8.94E-03	6.73E-03	6.39E-03
ANTHRACENE	3.30E-03	3.20E-03	2.92E-03	6.02E-03	4.56E-03	3.92E-03
FLUORANTHENE	2.54E-03	2.50E-03	2.54E-03	2.45E-03	2.35E-03	1.92E-03
PYRENE	3.63E-03	2.20E-03	2.19E-03	3.33E-03	2.67E-03	2.22E-03
BENZO(a)ANTHRACENE	1.60E-04	2.00E-04	1.76E-04	2.04E-04	1.78E-04	2.11E-04
CHRYSENE	8.80E-05	8.28E-05	6.96E-05	7.03E-05	6.32E-05	7.08E-05
BENZO(b)FLUORANTHENE	2.47E-05	2.07E-05	1.81E-05	1.66E-05	2.27E-05	1.97E-05
BENZO(k)FLUORANTHENE	1.78E-05	2.52E-05	2.07E-05	1.74E-05	2.30E-05	2.74E-05
BENZO(a)PYRENE	3.66E-05	3.78E-05	6.05E-05	6.56E-05	6.43E-05	6.12E-05
INDENO(1,2,3-cd)PYRENE	2.14E-05	2.14E-05	4.57E-05	1.14E-05	2.00E-05	5.71E-06
DIBENZO(a,h)ANTHRACENE	1.81E-05	1.81E-05	1.65E-05	1.81E-05	1.48E-05	1.32E-05
BENZO(ghi)PERYLENE	1.75E-05	1.17E-05	1.46E-05	9.72E-06	1.75E-05	5.83E-06
TOTAL PAH	1.08E-01	1.13E-01	1.10E-01	1.00E-01	1.39E-01	1.25E-01

Table A-3. Average concentrations of PAHs in sediment and aqueous phases after equilibration with M85.

	Average Sediment Phase Concentration (mg/kg)				Average Aqueous Phase Concentration (mg/L)			
	Control 0.500	M-85 present 0.459 M-1s	1st dilution 0.184 M-2s	2nd dilutio 0.0735 M-3s	Control 0.500	M-85 present 0.459 M-1a	1st dilution 0.184 M-2a	2nd dilutio 0.0735 M-3a
methanol								
Volume fraction (f)								
Sample								
naphthalene	97.8	91.7	90.4	85.5	6.54E+00	3.74E+00	3.03E-01	1.09E-01
2-methylnaphthene	85.6	83.5	85.6	85.2	4.97E-01	3.34E-01	2.75E-02	9.88E-03
1-methylnaphthene	84.5	77.8	87.0	74.3	3.95E-01	2.37E-01	3.08E-02	9.16E-03
acenaphthylene	25.4	27.4	24.6	25.0	1.47E-01	6.91E-02	6.53E-03	2.48E-03
acenaphthene	34.7	23.4	24.3	21.1	1.58E+00	7.40E-01	4.44E-02	1.23E-02
fluorene	36.4	28.8	27.1	28.0	6.66E-01	2.01E-01	3.18E-02	7.74E-03
phenanthrene	86.6	78.4	84.2	75.2	1.68E+00	8.97E-01	4.26E-02	1.33E-02
anthracene	25.5	30.6	30.2	28.3	6.33E-01	5.97E-01	3.35E-02	9.40E-03
fluoranthene	56.7	52.2	55.3	51.9	7.70E-01	5.52E-01	2.79E-02	5.30E-03
pyrene	98.2	96.3	95.9	93.4	9.18E-01	4.72E-01	2.95E-02	6.44E-03
benzo(a)anthracene	40.3	29.1	33.0	30.7	2.10E-01	5.70E-02	1.97E-03	3.63E-04
chrysene	40.1	35.0	38.2	28.5	1.03E-01	3.63E-02	7.92E-04	1.45E-04
benzo(b)fluoranthene	20.5	24.3	30.6	26.4	4.72E-02	1.28E-02	4.68E-04	6.51E-05
benzo(k)fluoranthene	17.8	20.6	21.0	16.1	6.17E-02	1.51E-02	5.33E-04	6.46E-05
benzo(a)pyrene	22.4	37.3	44.9	34.5	1.13E-01	3.08E-02	1.12E-03	1.79E-04
indeno(1,2,3-cd)pyrene	17.6	26.6	29.5	24.7	2.67E-02	1.53E-02	6.10E-04	7.03E-05
dibenzo(a,h)anthracene	10.6	7.41	7.51	8.14	2.11E-02	1.01E-02	3.30E-04	4.74E-05
benzo(ghi)perylene	18.6	15.8	15.0	15.1	2.15E-02	7.90E-03	2.33E-04	3.33E-05
Total PAH	819	771	809	752	14.4	8.03	0.583	0.186

Table A-4. Average concentrations of PAHs in sediment and aqueous phases after equilibration with E85.

ethanol Volume fraction (f) Sample	Average Sediment Phase Concentration (mg/kg)				Average Aqueous Phase Concentration (mg/L)			
	Control	E-85 present	1st dilution	2nd dilution	Control	E-85 present	1st dilution	2nd dilution
	0.500	0.459 E-1s	0.184 E-2s	0.0735 E-3s	0.500	0.459 E-1a	0.184 E-2a	0.0735 E-3a
naphthalene	84.0	93.0	94.5	92.7	6.45E+00	4.47E+00	3.43E-01	1.32E-01
2-methylnaphthene	81.1	89.7	89.4	100.6	4.75E-01	2.99E-01	3.08E-02	1.29E-02
1-methylnaphthene	82.6	71.8	75.7	83.4	4.89E-01	2.20E-01	2.66E-02	1.04E-02
acenaphthylene	21.8	20.7	21.6	23.1	1.69E-01	1.81E-01	6.42E-03	2.15E-03
acenaphthene	32.4	33.0	30.0	36.3	1.35E+00	9.87E-01	5.41E-02	2.42E-02
fluorene	35.8	33.5	34.7	38.2	1.15E+00	7.58E-01	3.67E-02	1.19E-02
phenanthrene	88.1	81.8	88.8	88.3	1.43E+00	9.37E-01	6.65E-02	1.62E-02
anthracene	40.7	33.3	32.3	32.8	1.10E+00	5.17E-01	5.06E-02	9.97E-03
fluoranthene	61.2	52.2	55.4	58.6	1.03E+00	5.76E-01	2.62E-02	5.82E-03
pyrene	85.0	83.7	87.5	90.7	8.78E-01	4.92E-01	2.79E-02	6.17E-03
benzo(a)anthracene	37.6	28.4	30.8	31.6	1.19E-01	7.67E-02	1.65E-03	4.06E-04
chrysene	34.3	27.3	32.9	28.4	7.43E-02	3.37E-02	8.50E-04	1.65E-04
benzo(b)fluoranthene	21.6	24.4	27.1	32.0	3.35E-02	4.01E-02	4.04E-04	9.93E-05
benzo(k)fluoranthene	15.3	12.9	16.0	16.2	3.36E-02	3.29E-02	3.63E-04	7.58E-05
benzo(a)pyrene	21.9	28.6	27.4	29.6	6.57E-02	4.69E-02	8.86E-04	1.70E-04
indeno(1,2,3-cd)pyrene	13.1	12.4	14.1	14.3	2.06E-02	1.21E-02	2.64E-04	4.37E-05
di benzo(a,h)anthracene	9.27	6.36	7.26	7.69	3.51E-02	8.83E-03	2.52E-04	4.47E-05
benzo(ghi)perylene	19.9	14.2	16.3	15.3	3.02E-02	1.69E-02	2.81E-04	3.13E-05
Total PAH	786	747	782	820	14.9	9.70	0.674	0.233

Table A-5. Average concentrations of PAHs in sediment and aqueous phases after equilibration with oxygenated gasoline.

MTBE Volume fraction (f) Sample	Average Sediment Phase Concentration (mg/kg)				Average Aqueous Phase Concentration (mg/L)			
	Control 0.0584	MTBE present 0.0584 OG-1s	1st dilution 0.0234 OG-2s	2nd dilution 0.00935 OG-3s	Control 0.0584	MTBE present 0.0584 OG-1a	1st dilution 0.0234 OG-2a	2nd dilution 0.00935 OG-3a
naphthalene	96.5	84.0	85.9	90.9	1.20E-01	1.01E-01	6.61E-02	6.50E-02
2-methylnaphthene	85.2	91.4	98.2	73.2	9.32E-03	1.03E-02	6.36E-03	4.52E-03
1-methylnaphthene	75.5	83.7	78.1	74.9	7.93E-03	9.02E-03	4.76E-03	4.52E-03
acenaphthylene	25.0	23.4	18.1	20.0	2.23E-03	2.52E-03	1.02E-03	9.82E-04
acenaphthene	31.8	39.9	37.7	39.6	1.72E-02	2.11E-02	1.21E-02	1.09E-02
fluorene	42.0	41.0	31.5	36.9	1.11E-02	1.06E-02	5.09E-03	5.53E-03
phenanthrene	82.0	88.2	79.9	89.0	1.22E-02	1.50E-02	7.49E-03	7.09E-03
anthracene	25.4	31.8	25.1	30.5	6.80E-03	9.83E-03	4.22E-03	4.55E-03
fluoranthene	50.3	44.7	48.0	49.4	4.58E-03	4.19E-03	2.29E-03	2.13E-03
pyrene	91.0	89.7	89.8	87.8	5.75E-03	4.90E-03	2.96E-03	2.93E-03
benzo(a)anthracene	40.7	38.8	32.6	38.4	4.48E-04	4.35E-04	1.90E-04	1.85E-04
chrysene	38.8	33.0	28.1	32.5	1.79E-04	1.52E-04	6.86E-05	7.03E-05
benzo(b)fluoranthene	28.6	30.4	22.3	28.2	6.37E-05	6.58E-05	2.18E-05	2.54E-05
benzo(k)fluoranthene	16.6	18.6	11.9	13.2	5.70E-05	6.38E-05	1.76E-05	1.81E-05
benzo(a)pyrene	32.9	40.1	29.9	35.0	1.62E-04	2.00E-04	7.35E-05	7.25E-05
indeno(1,2,3-cd)pyrene	14.6	16.9	6.6	8.1	3.30E-05	3.50E-05	7.87E-06	7.42E-06
dibenzo(a,h)anthracene	13.6	13.0	9.2	14.2	6.92E-05	6.51E-05	2.20E-05	2.88E-05
benzo(ghi)perylene	19.4	20.9	10.1	14.2	3.36E-05	3.32E-05	8.56E-06	9.21E-06
Total PAH	791	809	733	762	0.198	0.190	0.113	0.109

Table B-1. Estimated colloid/water partition coefficients in various fuel/water systems.

	M85/water		E85/water		Oxygenated Gasoline/water		Control
	log Kcol,m	log Kcol,w	log Kcol,m	log Kcol,w	log Kcol,m	log Kcol,w	
NAPHTHALENE	3.107	4.295	2.887	3.970	2.908	3.046	3.161
2-METHYLNAPHTHALENE	2.921	4.158	2.868	4.039	2.796	2.931	3.289
1-METHYLNAPHTHALENE	2.888	4.280	3.046	4.328	3.003	3.158	3.270
ACENAPHTHYLENE	2.960	4.002	3.013	3.930	3.119	2.917	3.301
ACENAPHTHENE	3.094	4.430	2.767	3.959	2.862	3.055	3.093
FLUORENE	3.103	4.512	3.046	4.260	3.081	3.303	3.274
PHENANTHRENE	3.021	4.475	2.935	4.202	2.862	3.026	3.248
ANTHRACENE	3.033	4.410	3.013	4.239	2.904	3.137	3.373
FLUORANTHENE	3.090	4.628	2.937	4.314	3.005	3.212	3.230
PYRENE	3.154	4.685	2.896	4.275	2.704	2.878	3.395
BENZO(a)ANTHRACENE	3.155	5.087	3.085	4.784	3.040	3.260	3.428
CHRYSENE	3.221	5.189	3.022	4.762	2.960	3.206	3.407
BENZO(b)FLUORANTHENE	3.296	5.378	3.111	5.154	3.045	3.335	3.469
BENZO(k)FLUORANTHENE	3.246	5.362	3.238	5.162	2.986	3.215	3.562
BENZO(a)PYRENE	3.225	5.277	3.232	5.136	3.022	3.323	3.610
INDENO(1,2,3-cd)PYRENE	3.273	5.598	3.138	5.433	2.992	3.652	3.580
DIBENZO(a,h)ANTHRACENE	3.279	5.359	3.191	5.209	3.083	3.518	3.517
BENZO(ghi)PERYLENE	3.355	5.702	3.212	5.360	3.073	3.588	3.501

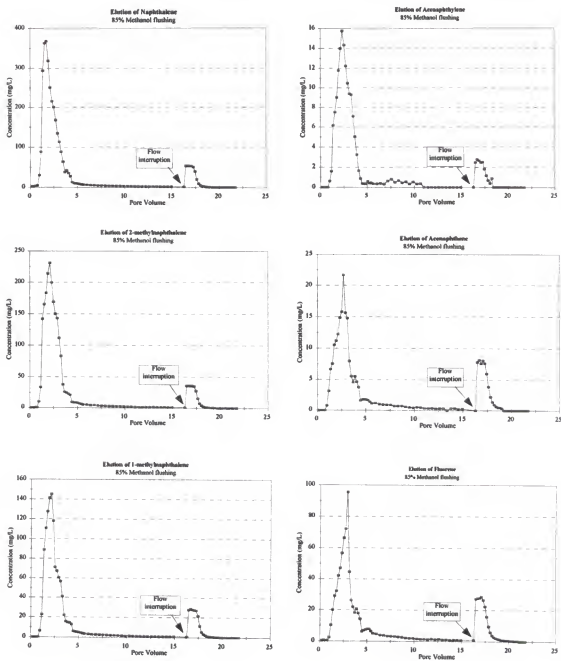


Figure C-1. Elution profile of PAHs by methanol flushing.

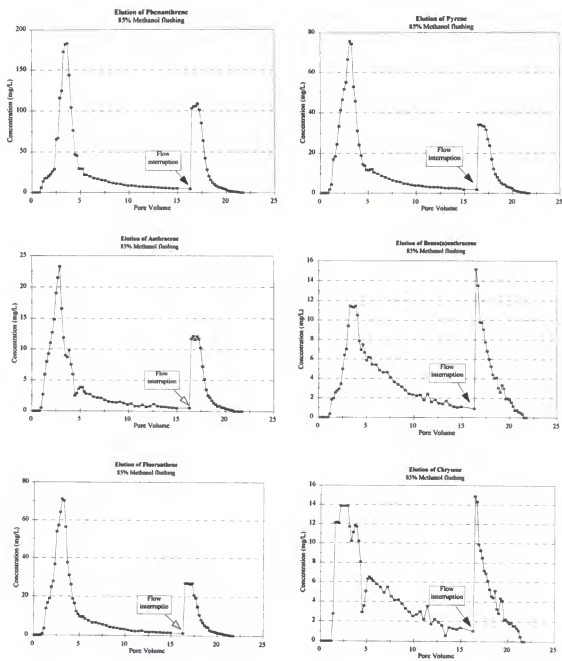


Figure C-1. (Continued).

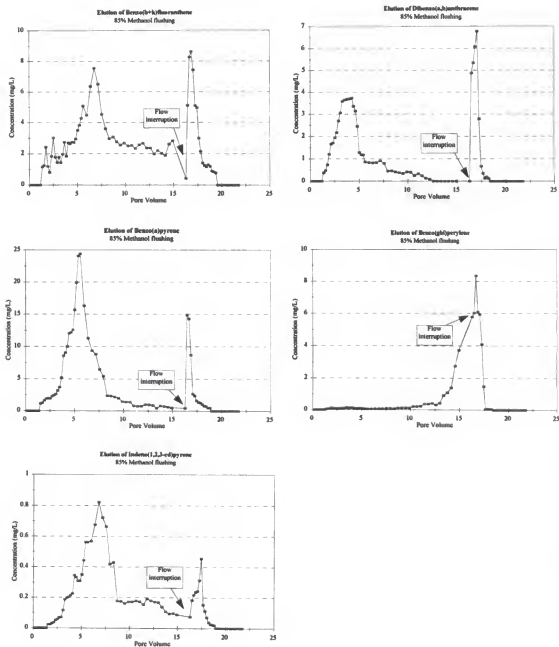


Figure C-1. (Continued).

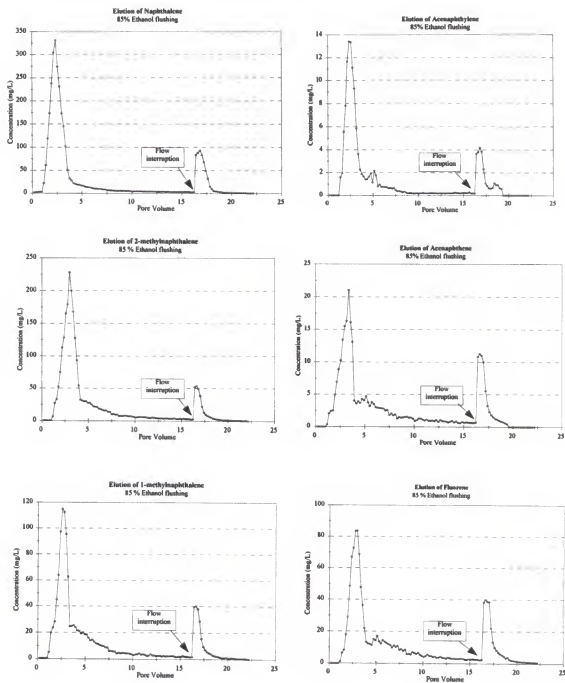


Figure C-2. Elution profile of PAHs by ethanol flushing.

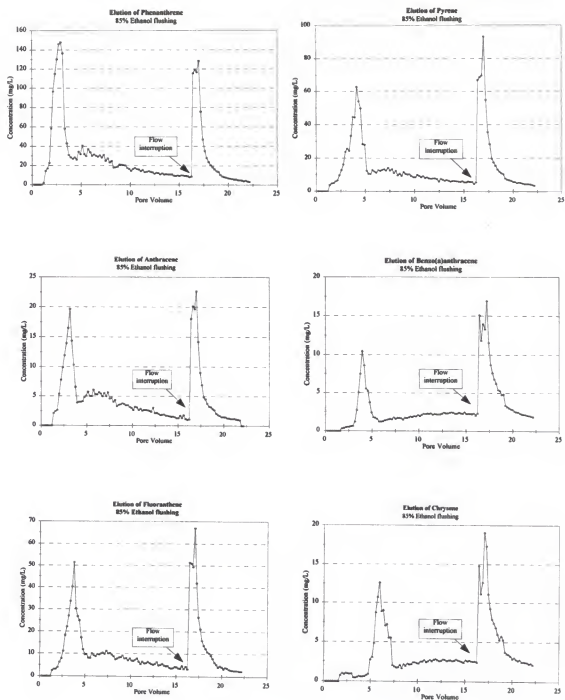


Figure C-2. (Continued).

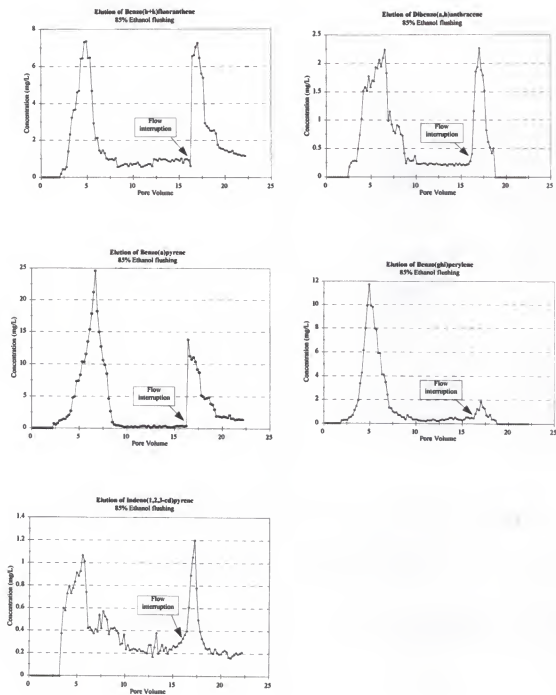


Figure C-2. (Continued).

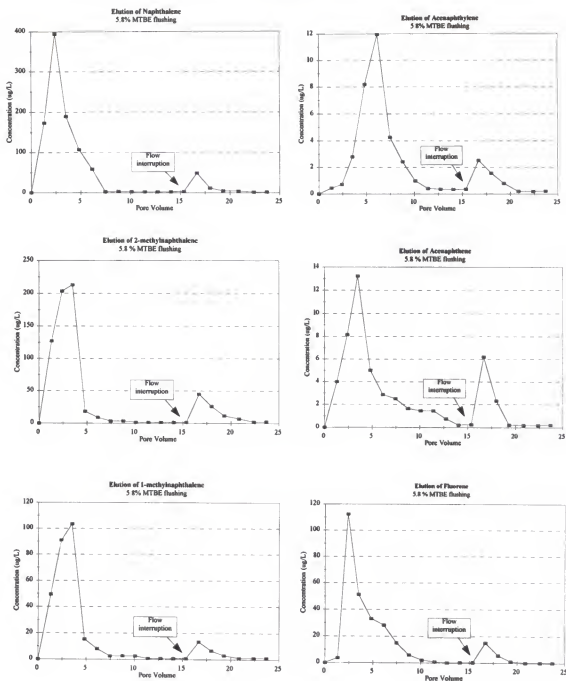


Figure C-3. Elution profile of PAHs by MTBE flushing.

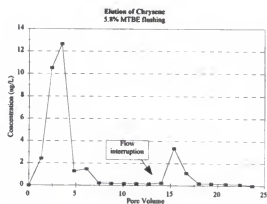
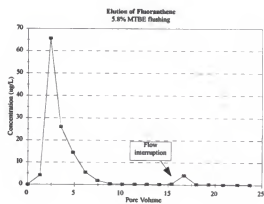
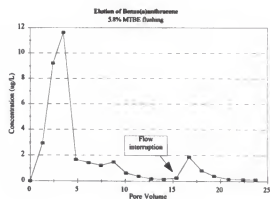
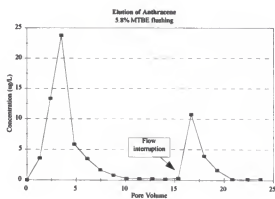
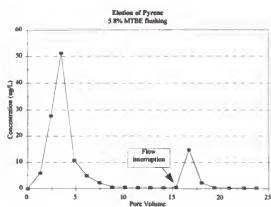
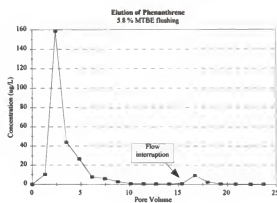


Figure C-3. (Continued).

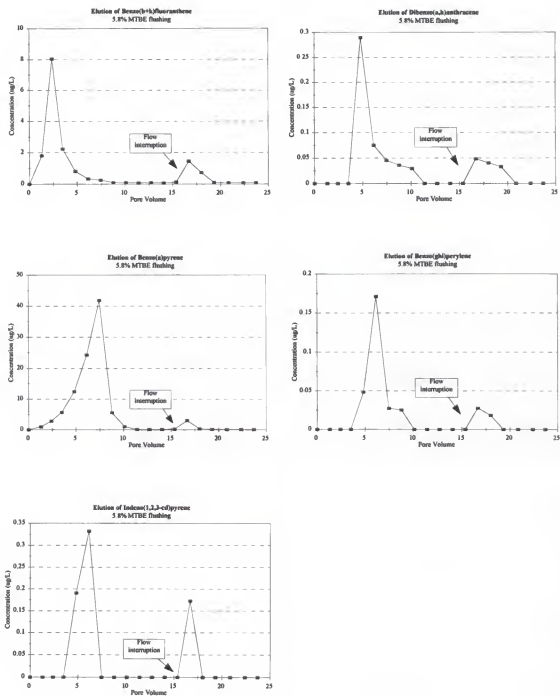


Figure C-3. (Continued).

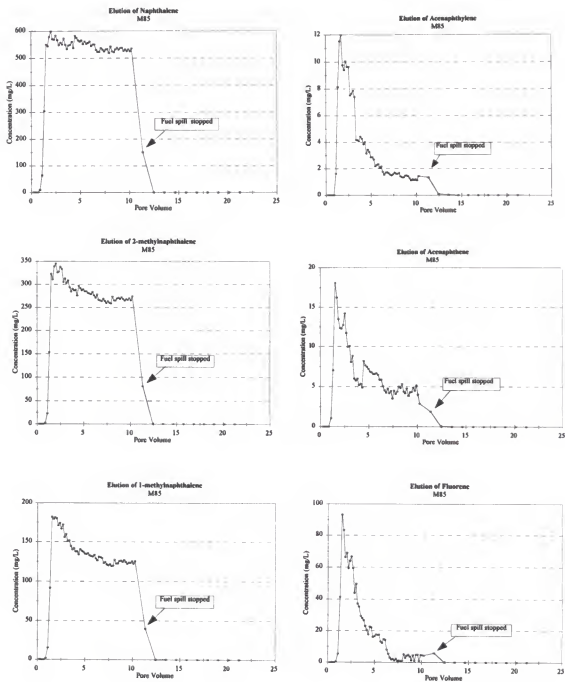


Figure C-4. Elution profile of PAHs due to spill of M85.

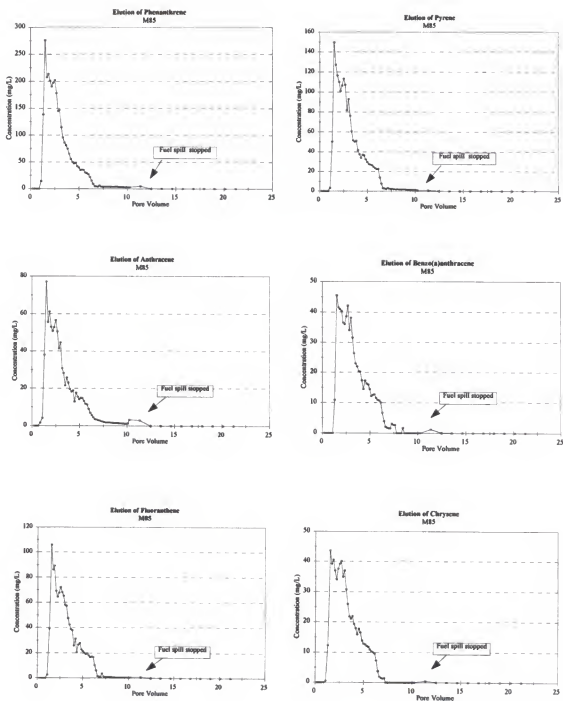


Figure C-4. (Continued).

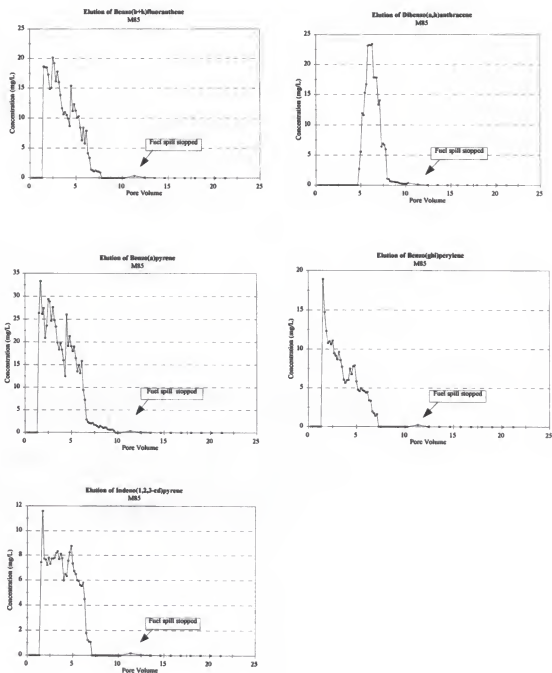


Figure C-4. (Continued).

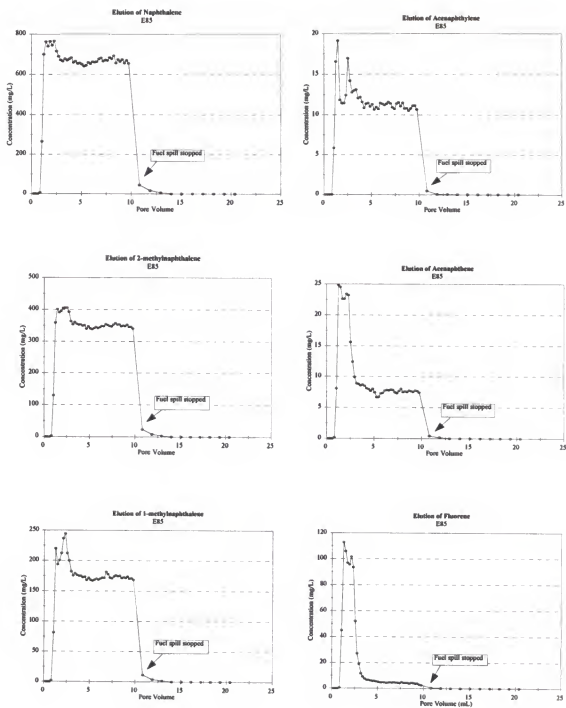


Figure C-5. Elution profile of PAHs due to spill of E85.

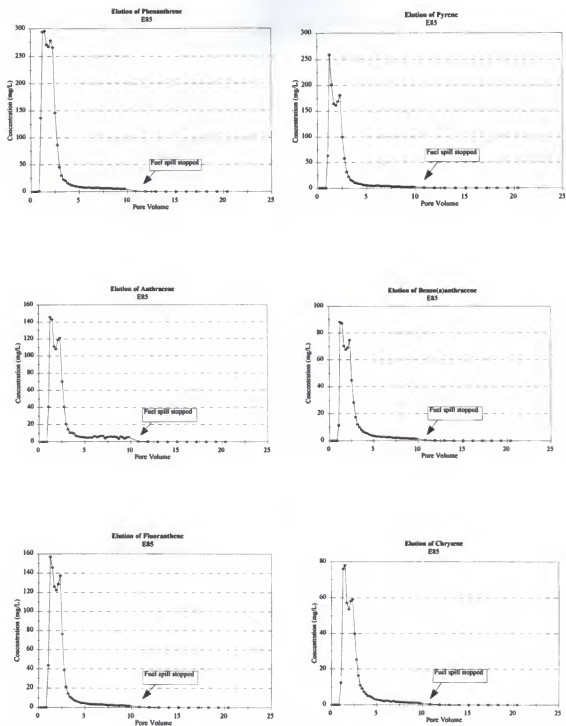


Figure C-5. (Continued).

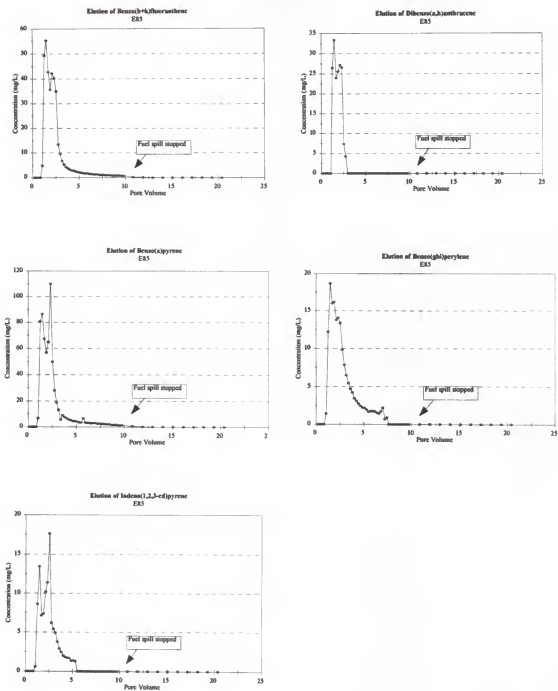


Figure C-5. (Continued).

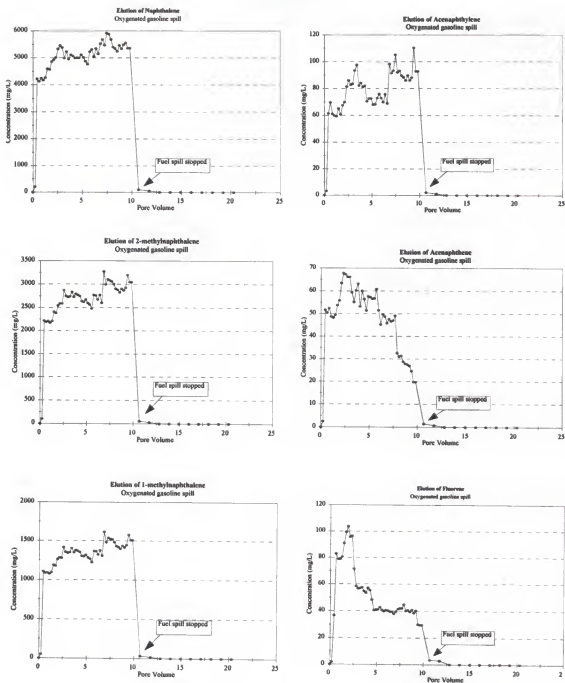


Figure C-6. Elution profile of PAHs due to spill of oxygenated gasoline.

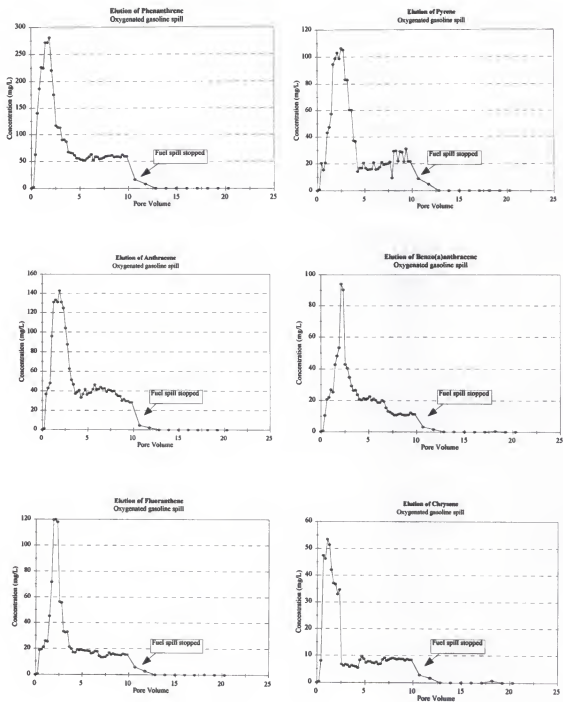


Figure C-6. (Continued).

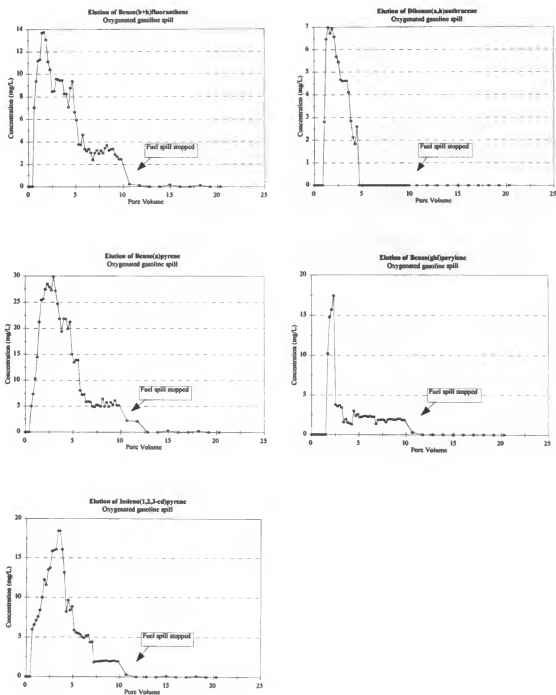


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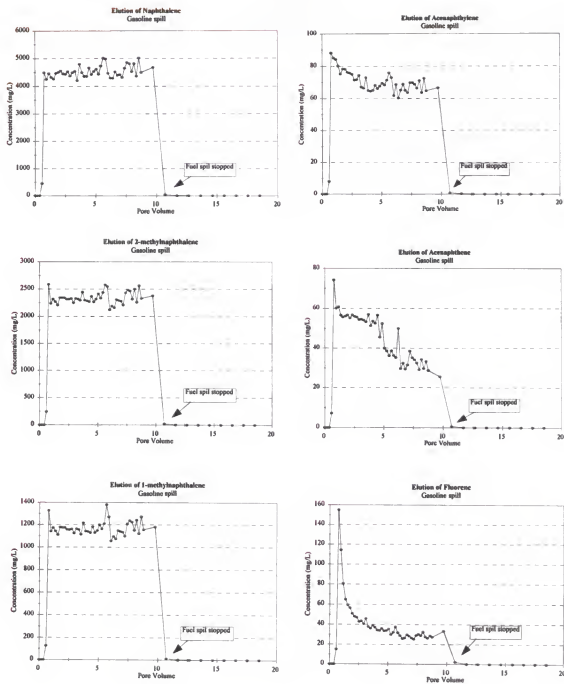


Figure C-7. Elution profile of PAHs due to spill of gasoline.

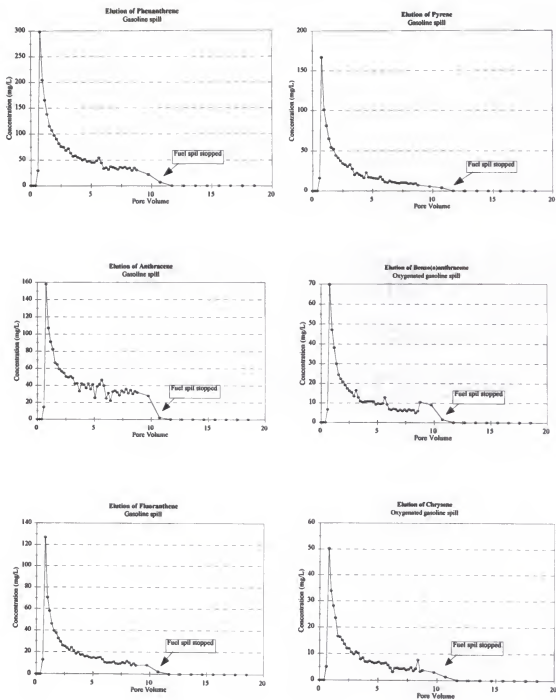


Figure C-7. (Continued).

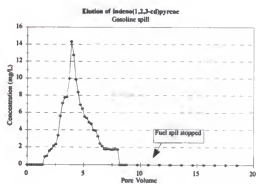
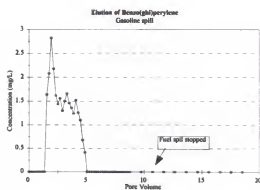
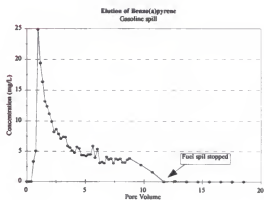
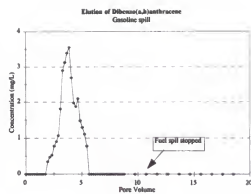
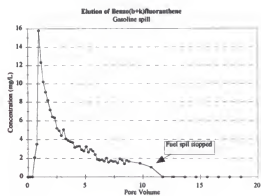


Figure C-7. (Continued).

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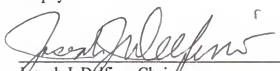
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BIOGRAPHICAL SKETCH

Colin Shih-Hsien Chen was born in Taipei, Taiwan, on December 21, 1962. He attended National Taiwan University and graduated with a Bachelor of Science degree in June, 1985. After two years of military service, he worked for 18 months as an environmental chemist in the Graduate Institute of Environmental Engineering, National Taiwan University. He continued his education at the University of Florida in 1989, and received the Master of Science degree in 1993. He is now completing work for his Doctor of Philosophy degree in environmental engineering sciences at the University of Florida.

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Joseph J. Delfino, Chair
Professor of Environmental Engineering
Sciences

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P. Suresh C. Rao, Cochair
Graduate Research Professor of Soil and
Water Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Paul A. Chadik
Assistant Professor of Environmental
Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Michael D. Annable
Assistant Professor of Environmental
Engineering Sciences

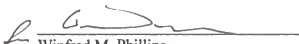
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Robert T. Kennedy
Associate Professor of Chemistry

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1996



Winfred M. Phillips
Dean, College of Engineering

Karen A. Holbrook
Dean, Graduate School